4.0 SUMMARY AND CONCLUSIONS

Researchers at CE-CERT and SAPRC at the University of California, Riverside and the Department of Toxicology at the University of California, Davis have completed a program to assess the potential impact of diesel fuel formulation on the speciation and toxic components of diesel exhaust. The test bed was a Cummins L10 engine operating over the heavy-duty transient test cycle using three diesel fuels: a pre-1993 diesel fuel, a low aromatic diesel fuel, and an alternative formulation diesel fuel.

The data quality objectives were to determine the magnitudes of the differences in toxic emissions and their variability among the different fuel types. For each fuel, the objectives were to:

- Measure all regulated emissions: THC, CO, CO_2, NOx, total particulates
- Quantify the mass fraction of the particulate below 10 and 2.5 μm aerodynamic diameter
- Collect, identify, and quantify at least 80% of the C_1-C_{12} VOC emissions
- Collect, identify, and quantify at least 80% of carbonyl compounds
- Collect, identify and quantify the elemental and inorganic ion components in the particulate
- Quantify the elemental and inorganic carbon fractions of the particulate
- Collect, identify and quantify the particulate-bound PAH and nitro-PAH emissions
- Collect, identify, and quantify the gas-phase PAH and nitro-PAH emissions
- Determine mutagenicity

and, for the pre-1993 and reformulated fuel to:

- Collect, identify, and quantify the nitrosamine emissions
- Collect, identify, and quantify the dioxins for analytical method development

All of these objectives were met. Multiple samples were collected during multi-day testing for each of the three fuels. A total of 47 test cycles (7 cold and 40 hot) were run with the pre-1993 diesel fuel, 23 test cycles (4 cold and 19 hot) were run with the low aromatic diesel fuel, and 39 test cycles (5 cold and 34 hot) were run with the reformulated diesel blend. Specific conclusions from the study are summarized below:

THC, CO, NOx, and PM

- THC and NOx show the following order of emission rate with fuel type for both the cold- and hot-start cycles: pre-1993>reformulated>low aromatic. All of these differences were statistically significant at the 95% confidence level.

- Reductions in NOx emission rates with the low aromatic and reformulated fuels range from 2.6 to 7.6%.

- Cold-start THC emissions were reduced by 27% with the low aromatic fuel and 16% with the reformulated fuel, while hot-start THC emissions were reduced by 7.6 and 3.8% with the low aromatic and reformulated fuels, respectively.

- The low aromatic fuel shows an increase and the reformulated fuel a decrease in CO emission rates compared to the pre-1993 fuel; none of these differences were significant at the 95% confidence level.

- Both the low aromatic (8.9%) and the reformulated (2.7%) fuels show increases in hot-start CO emissions compared to the pre-1993 fuel which are statistically significant at the 95% confidence level.

- The low aromatic and reformulated fuels have the largest impact on PM emission rates, with reductions ranging from17 to 25% compared to the pre-1993 fuel. These reductions in PM emission rates are statistically significant at the 95% confidence level, but there is not a statistically significant difference between the low aromatic and reformulated fuels.

- There are significant differences between this study and the CARB certification procedure, which do not allow conclusions with regard to whether the reformulated fuel meets the certification requirements. These include the use of a difference engine test bed than that

specified for certification and a lower aromatic content and higher cetane number for the low aromatic fuel used in this study compared to baseline low aromatic fuel used for certification.

PM_{10} and $PM_{2.5}$

- Greater than 99% of the particulate mass is smaller than 10μm aerodynamic diameter and greater than 95% is smaller than 2.5 μm aerodynamic diameter.

- No significant differences in PM_{10} and $PM_{2.5}$ size distributions were found as a function of fuel type.

Elemental and Organic Carbon, Ion, and Elemental Analyses

- Elemental and organic carbon dominate the composition of the particulate matter for all fuels, representing more than 97% of the total identified mass.

- Organic carbon as percent of total carbon is relatively constant for all three fuels and ranges from 33 to 40%.

- The low aromatic and reformulated fuels show lower total carbon emission rates than the pre-1993 fuel associated with their lower total PM emission rates.

- Nitrate emission rates are higher for the low aromatic and reformulated fuels than for the pre-1993 fuel. This may result from use of organonitrates as cetane improvers for the reformulated fuel, but is unexplained for the low aromatic fuel.

- Sulfur and sulfate emission rates follow the trend pre-1993 > reformulated > low aromatic. This is the same order as the fuel sulfur level.

- Mg, P, Ca, and Zn emission rates are relatively constant for the different fuels and are derived from the oil.

- The oil derived components and Fe (due to engine wear) have higher emission rates during cold-start than hot-start.

- Si emission rates are relatively constant for all fuels and both cold- and hot-cycles with the source of these emissions being unknown.

Carbonyls

- All three fuels show the same trend in emission rates for carbonyls: formaldehyde > acetaldehyde > acrolein > propionaldeyde.

- Emission rates during cold- and hot-start are very similar.

- Low aromatic fuel has lower formaldehyde and acetaldehyde emission rates than the pre-1993 and reformulated fuel during cold-start, which are statistically significant at the 95% confidence level. These differences are, however, less than 20% and are not observed during hot-start.

- The pre-1993 fuel has approximately 10% lower acetaldehyde emissions than the low aromatic and reformulated fuels during hot-start which are statistically significant at the 95% confidence level.

- The low aromatic fuel shows an increase in acrolein emissions during cold- and hot-start compared to the pre-1993 and reformulated fuels. These results are statistically significant at the 95% confidence level.

Speciated Hydrocarbons

- All fuels show the same emission trends for the gas phase hydrocarbons. Benzene emission rates ranged from 5.65-8.15 mg/Bhp-hr with 1,3-butadiene, toluene, o-xylene, m&p-xylene, styrene, and naphthalene emission rates at or below 2.5 mg/Bhp-hr.

- The low aromatic fuel has higher hot-start 1,3-butadiene, higher hot- and cold-start benzene, higher hot-start toluene, lower cold-start o-xylene, and lower hot-start m&p-xylene emissions than the other fuels. All of these differences are statistically significant at the 95% confidence level.

- No statistically significant differences were observed between the pre-1993 and reformulated fuels.

Particle-Bound PAH

- The high-volume sampling system employed by SAPRC and consisting of Teflon-impregnated glass fiber filters backed by two polyurethane foam plugs (PUF) in series allowed quantitative sampling of PAH with molecular weights ≥178 Daltons. The PAH of molecular weights ≥228 Daltons were found only on the filters. The PAH of molecular weights between 178 and 202 Daltons were distributed between the filters and the front PUFs. Breakthrough of 2,3,5-trimethylnaphthalene onto the back PUF occurred, and the values measured for this alkyl-PAH with the SAPRC sampling system must be strictly viewed as lower limits to the total emissions.

- The most dramatic differences in emission rates of particle-bound PAH with fuel type occurred for the alkyl-PAH, 2,3,5-trimethylnaphthalene and the methylphenanthrenes, and the emission rate rankings followed the PAH content of the fuels. That is, the highest emissions of the alkyl-PAH were from the pre-1993 fuel, followed by the reformulated blend fuel and the lowest emissions were from the low aromatic fuel. These fuel differences were highly significant for all fuel pairwise comparisons.

- The trend in alkyl-PAH emissions with fuel PAH content for the particle-bound alkyl-PAH is consistent with the trend observed for the emissions of gas-phase alkylnaphthalenes.

- Phenanthrene was the most abundant PAH measured by the SAPRC sampling system for the pre-1993 and reformulated blend fuels. In the low aromatic fuel emissions, phenanthrene was second only to pyrene. For the pre-1993 fuel, the emissions of the methylphenanthrenes were comparable to that of phenanthrene. For the reformulated blend fuel, the methylphenanthrene emissions were approximately half the phenanthrene emissions, while for the low aromatic fuel, the methylphenanthrene emissions were <20% of the phenanthrene emissions. This suggests that a significant portion of the alkyl-PAH emissions are due to unburned fuel components and that the PAH formed during the combustion process are generally unsubstituted PAH.

- For the unsubstituted PAH with four and more rings, all fuels showed the same emission trends with pyrene being the most abundant PAH measured, followed by fluoranthene and benzo[ghi]perylene. Ten PAH showed no statistically significant difference in emission rate with fuel type. These ten PAH were: fluoranthene, pyrene, cyclopenta[cd]pyrene,

benzo[b+j+k]fluoranthenes, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, and dibenzo[a,h+a,c]-anthracene.

- Ten PAH showed statistically higher emission rates from the pre-1993 fuel than from either the reformulated or low aromatic fuel, but showed no difference between the latter two fuels. These ten PAH were: phenanthrene, anthracene, benzo[c]phenanthrene, benzo[ghi]fluoranthene, benz[a]anthracene, chrysene + triphenylene, indeno[1,2,3-cd]fluoranthene, benzo[c]chyrsene, dibenz[a,j]anthracene, and dibenzo[a,h]pyrene.

- Benzo[b]chrysene was the only PAH other than the alkyl-PAH which showed significant differences between all three fuel pairs and, as with the alkyl-PAH, the ranking of the emission rates was: pre-1993 fuel highest, reformulated blend intermediate and low aromatic fuel lowest.

- For dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, and dibenzo[a,i]pyrene, the low aromatic fuel emission rates were significantly lower than both the pre-1993 and reformulated blend fuels, which were not different from one another. For coronene, the pre-1993 fuel had significantly higher emissions than the low aromatic fuel.

- In all cases where there was a statistically significant difference between the low aromatic fuel PAH emission rate and one or both of the other fuels, the low aromatic fuel PAH emission rate was always lower.

- The lowered emissions of volatile alkyl-PAH with decreased fuel PAH content may be expected to lead to a decreased potential for the atmospheric formation of mutagenic nitro-PAH and nitro-PAH lactones.

Nitro-PAH

- 1-Nitropyrene, 6-nitrobenzo[a]pyrene, 9-nitroanthracene, and 1- and 2-nitronaphthalene were measured in the emissions of all three fuel types. 1-Nitropyrene was the most abundant nitro-PAH measured. The nitronaphthalenes were found in the PUF extracts, while the other nitro-PAH were particle-bound.

- There was no statistically significant difference in the emission rates with fuel type for 1-nitronaphthalene, 1-nitropyrene and 6-nitrobenzo[a]pyrene. 9-Nitroanthracene was lower in the reformulated fuel emissions than either the low aromatic or pre-1993 fuels. The low aromatic fuel had lower emission rates of 2-nitronaphthalene than the pre-1993 and reformulated fuels.

Vapor-Phase PAHs

- Methylnaphthalene, 2,6-dimethylnaphthalene, and trimethylnaphthalene were emitted at the highest level in the pre-1993 fuel followed by the reformulated blend and lowest in the low aromatic fuel.

- Naphthalene emission rates were the highest of all vapor phase PAHs for all three fuels.

- All the targeted vapor phase PAHs except acenaphthene were detected in the exhaust of all three fuels.

Nitrosamine Analyses for Pre-1993 and Reformulated Blend Fuels

- The pre-1993 emission rate for N-nitrosodimethylamine was 6.41 µg/Bhp-hr and for the reformulated blend was 7.92 µg/Bhp-hr.

- N-nitrosodipropylamine was detected in the emissions of the pre-1993 and reformulated blend fuels.

- N-nitrosomorpholine was not detected in the emissions of the pre-1993 and reformulated fuels.

Dioxins Analyses for Pre-1993 and Reformulated Blend Fuels

- PCDDs and PCDFs were detected in the emissions from the reformulated blend and pre-1993 fuel.

- The most toxic isomers, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF were not detected in the emissions of the pre-1993 and the reformulated blend.

- TEQ profiles were incomplete due to the low level of PCDD and PCDF detected in the emission samples. This was the case even though detection limits were estimated to be 7-10 times lower than the EPA recommended 100 pg TEQ per liter of fuel target detection level.

Bioassay

- Mutagenic activity was detected in the particle and vapor-phase emissions from all fuels tested.

- The pre-1993 fuel has higher specific mutagenic activity (activity per mg particulate matter or per vapor-phase extract) than the emissions from low aromatic and reformulated blend fuels.

- Higher mutagen emission values (mutagenic activity per brake-horsepower hr) were observed in the particle and vapor-phase collected from pre-1993 fuel than in the low aromatic and reformulated blend fuels.

- Mutagenic activity of HPLC fractions provided mutagenic profiles or "mutagrams" of each fuel type and the most mutagenic fraction for the particulate matter is in a fraction that is different from the fractions where the PAHs and nitro-PAHs are present. For all fuels, one fraction accounts for approximately 60-70% of the total activity (+S9) and two fractions account for approximately 70-80% of activity without metabolic enzymes added (-S9).

5.0 RECOMMENDATIONS

This study was designed to determine the effects of diesel toxicity and to test sampling methods for non-criteria pollutants emitted from a single heavy duty engine and cycle operating on different diesel formulations. The value of the results obtained would be enhanced by the inclusion of a variety of engine types and operating conditions.

PAH and nitro-PAH were observed in the emissions from all three fuel types and additional data should be obtained for these species employing a variety of engine types, and driving conditions.

To obtain complete TEQ profiles for dioxins additional methods development is required, perhaps including larger sample sizes. A reformulated fuel high in chlorine should be tested to determine the worst case emissions for PCDDs and PCDFs.

Additional nitrosamine data should be obtained employing a variety of engine types, and driving conditions.

The most mutagenic fractions of the diesel exhaust extracts should be further chemically characterized and the mutagenic compounds isolated and identified.

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ATTACHMENT A

Table A1. Emission Test Results with Cummins L10 Engine using Pre-1993 Fuel

Test Date	12/2/96	12/2/96	12/2/96	12/2/96
Test Number	337CS	337H1	337H2	337H3
Cycle Type	Cold	Hot 1	Hot 2	Hot 3
Emissions (g/Bhp-hr.)				
NO_X	4.89	4.53	4.61	NA
THC	0.53	0.52	0.48	NA
CO	2.47	2.43	2.34	NA
CO_2	552.5	519.6	518.2	NA
Particulate	0.237	0.218	0.206	NA
BSFC (Lb./Bhp-hr.)	0.394	0.371	0.364	NA
Work (Bhp-hr.)	22.282	22.379	22.417	NA

Test Date	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96	12/3/96
Test Number	338cs	338H1	338H2	338H3	338H4	338H5	338H6	338H7	338H8	338H9
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7	Hot 8	Hot 9
Emissions (g/Bhp-hr.)										
NO_X	5.09	4.72	4.87	4.77	4.75	4.74	4.8	4.77	4.73	4.74
THC	0.56	0.55	0.52	0.53	0.54	0.54	0.5	0.51	0.54	0.53
CO	2.4	2.32	2.24	1.77	1.79	2.32	2.36	2.39	2.4	2.36
CO_2	551.7	525.7	518.6	520.8	517.7	511.9	518.4	515.1	515.4	515.3
Particulate	0.257	0.231	0.218	0.212	0.212	0.208	0.206	0.201	0.202	0.2
BSFC (Lb./Bhp-hr.)	0.387	0.369	0.364	0.365	0.363	0.36	0.364	0.362	0.362	0.362
Work (Bhp-hr.)	22.336	22.391	23.37	22.402	22.414	22.397	22.397	22.412	22.431	22.417

Test Date	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96	12/4/96
Test Number	339CS	339H1	339H2	339H3	339H4	339H5	339H6	339H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	4.93	4.5	4.63	4.7	4.62	4.74	4.69	4.66
THC	0.58	0.54	0.48	0.53	0.52	0.51	0.51	0.51
CO	2.35	2.3	2.28	2.27	2.12	2.31	2.33	2.43
CO_2	552.7	526.8	523.6	522.1	518	520.8	527.3	522
Particulate	0.276	0.232	0.22	0.222	0.212	0.223	0.218	0.228
BSFC (Lb./Bhp-hr.)	0.388	0.37	0.368	0.367	0.364	0.366	0.37	0.367
Work (Bhp-hr.)	22.283	22.375	22.391	22.361	22.399	22.399	22.417	22.417

Table A1-cont. Emission Test Results with Cummins L10 Engine using Pre-1993 Fuel

Test Date	12/5/96	12/5/96	12/5/96	12/5/96	12/5/96
Test Number	340CS	340H1	340H2	340H3	340H4
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4
Emissions (g/Bhp-hr.)					
NO_X	4.8	4.5	4.59	4.62	4.63
THC	0.53	0.5	0.51	0.54	0.54
CO	2.41	2.21	2.31	2.36	2.36
CO_2	549.7	520.7	520.7	521.9	521.5
Particulate	0.264	0.231	0.219	0.229	0.231
BSFC (Lb./Bhp-hr.)	0.386	0.366	0.366	0.367	0.366
Work (Bhp-hr.)	22.311	22.427	22.393	22.354	22.361

Test Date	12/6/96	12/6/96	12/6/96	12/6/96
Test Number	341CS	341H1	341H2	341H3
Cycle Type	Cold	Hot 1	Hot 2	Hot 3
Emissions (g/Bhp-hr.)				
NO_X	4.94	4.6	4.72	4.77
THC	0.58	0.53	0.53	0.53
CO	2.53	2.47	2.43	1.82
CO_2	553.2	521.3	519.3	520.8
Particulate	0.278	0.246	0.231	0.228
BSFC (Lb./Bhp-hr.)	0.389	0.366	0.365	0.365
Work (Bhp-hr.)	22.306	22.408	22.363	22.341

Test Date	1/8/97	1/8/97	1/8/97	1/8/97	1/8/97	1/8/97	1/8/97	1/8/97
Test Number	8CS	8H1	8H2	8H3	8H4	8H5	8H6	8H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	5.03	4.8	4.87	4.84	4.89	4.89	4.94	4.86
THC	2.39	0.54	0.55	0.54	0.54	0.53	0.53	0.52
CO	2.22	2.2	2.21	2.24	2.2	2.22	2.26	2.31
CO_2	536.2	509.8	514.6	513	514.7	515.5	515.8	512
Particulate	0.26	0.22	0.227	0.221	0.213	0.215	0.215	0.209
BSFC (Lb./Bhp-hr.)	0.376	0.356	0.361	0.36	0.361	0.362	0.362	0.36
Work (Bhp-hr.)	22.131	22.17	22.175	22.222	22.225	22.211	22.213	22.223

Table A1-cont. Emission Test Results with Cummins L10 Engine using Pre-1993 Fuel

Test Date	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97	1/9/97
Test Number	9CS	9H1	9H2	9H3	9H4	9H5	9H6	9H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	5.18	4.83	4.84	4.84	4.81	4.85	4.88	4.84
THC	0.55	0.52	0.54	0.52	0.53	0.54	0.5	0.52
CO	2.22	2.2	2.21	2.24	2.2	2.22	2.26	2.3
CO_2	534.9	509.7	520.2	517.3	513.4	515.3	513.7	515.1
Particulate	0.24	0.222	0.214	0.219	0.208	0.586	0.21	0.214
BSFC (Lb./Bhp-hr.)	0.376	0.358	0.365	0.363	0.36	0.362	0.361	0.361
Work (Bhp-hr.)	22.128	22.226	22.234	22.181	22.275	22.22	22.193	22.233

Table A2. Emission Test Results with Cummins L10 Engine using Low Aromatic Fuel

Test Date	12/9/96	12/9/96	12/9/96	12/9/96			
Test Number	344H1	344H2	344H3	344H4			
Cycle Type	Hot 1	Hot 2	Hot 3	Hot 4			
Emissions (g/Bhp-hr.)							
NO_X	4.31	4.45	4.49	4.36			
THC	0.43	0.49	0.48	0.48			
CO	2.46	2.43	2.46	2.48			
CO_2	516.9	509.6	507.9	504.6			
Particulate	0.213	0.182	0.187	0.187			
BSFC (Lb./Bhp-hr.)	0.367	0.362	0.361	0.359			
Work (Bhp-hr.)	22.012	21.962	21.931	91.936			
Test Date	12/10/96	12/10/96	12/10/96	12/10/96	12/10/96		
Test Number	345CS	348H1	345H2	345H3	345H5		
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4		
Emissions (g/Bhp-hr.)							
NO_X	4.67	4.31	4.39	4.41	4.45		
THC	0.4	0.5	0.5	0.48	0.5		
CO	2.47	2.34	2.46	2.43	2.46		
CO_2	545.9	519.1	513.2	513.7	511.3		
Particulate	0.195	0.18	0.178	0.178	0.177		
BSFC (Lb./Bhp-hr.)	0.388	0.369	0.365	0.365	0.363		
Work (Bhp-hr.)	21.957	21.954	21.979	21.936	21.978		
Test Date	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96	12/11/96
Test Number	346CS	346H1	346H2	346H3	346H4	346H5	346H6
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6
Emissions (g/Bhp-hr.)							
NO_X	4.56	4.37	4.45	4.38	4.48	4.35	4.37
THC	0.42	0.48	0.5	0.47	0.5	0.47	0.49
CO	2.47	2.45	2.42	2.43	2.43	2.48	2.48
CO_2	546.8	518.2	516	511.3	514.6	525.7	515.1
Particulate	0.195	0.18	0.175	0.179	0.176	0.186	0.181
BSFC (Lb./Bhp-hr.)	0.388	0.368	0.367	0.363	0.366	0.374	0.366
Work (Bhp-hr.)	21.998	22.02	22.043	22.047	22.963	21.978	21.955

Table A2-cont. Emission Test Results with Cummins L10 Engine using Low Aromatic Fuel

Test Date	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96	12/12/96	12/13/96
Test Number	347CS	347H1	347H2	347H3	347H4	347H5	347H6	348*
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	
Emissions (g/Bhp-hr.)								
NO_X	4.55	4.28	4.46	4.46	4.42	4.42	4.48	
THC	0.42	0.47	0.49	0.48	0.49	0.48	0.48	
CO	2.48	2.51	2.4	2.44	2.42	2.42	2.45	
CO_2	544	514.7	502.7	506.5	501.6	505.5	506.2	
Particulate	0.19	0.185	0.177	0.175	0.175	0.177	0.177	
BSFC (Lb./Bhp-hr.)	0.386	0.366	0.357	0.36	0.357	0.359	0.36	
Work (Bhp-hr.)	21.93	22.022	22.015	21.964	21.976	22.015	22.008	

* Test date was used to precondition engine for subsequent fuel sequence.

Table A3. Emission Test Results with Cummins L10 Engine using Reformulated Diesel Blend

Test Date	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96	12/16/96	
Test Number	351CS	351H1	351H2	351H3	351H4	351H5	351H6	
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	
Emissions (g/Bhp-hr.)								
NO_X	4.92	4.53	4.65	4.57	4.58	4.55	4.59	
THC	0.46	0.46	0.49	0.49	0.5	0.51	0.49	
CO	2.28	2.23	2.26	2.25	2.31	2.33	2.29	
CO_2	550.2	517.9	516.8	515.6	509.5	506.5	504.7	
Particulate	0.245	0.177	0.168	0.18	0.172	0.179	0.167	
BSFC (Lb./Bhp-hr.)	0.386	0.364	0.363	0.362	0.358	0.356	0.355	
Work (Bhp-hr.)	22.093	22.189	22.149	22.196	22.233	22.229	22.28	

Test Date	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96	12/17/96
Test Number	352CS	352H1	352H2	352H3	352H4	352H5	352H6	352H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	4.81	4.42	4.36	4.51	4.55	4.51	4.54	4.59
THC	0.51	0.47	0.48	0.5	0.5	0.49	0.49	0.5
CO	2.41	2.35	2.32	2.33	2.37	2.41	2.41	2.43
CO_2	551.2	516.9	511.3	513.5	512.9	510.1	507.8	510.2
Particulate	0.203	0.183	0.176	0.17	0.17	0.214	0.204	0.206
BSFC (Lb./Bhp-hr.)	0.387	0.363	0.359	0.361	0.36	0.358	0.357	0.359
Work (Bhp-hr.)	22.077	22.15	22.148	22.179	22.163	22.215	22.177	22.203

Test Date	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96	12/18/96
Test Number	353CS	353H1	353H2	353H3	353H4	353H5	353H6	353H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	4.82	4.52	4.48	4.57	4.59	4.66	4.68	4.74
THC	0.46	0.5	0.53	0.55	0.54	0.54	0.51	0.5
CO	2.27	2.24	2.2	2.27	2.27	2.28	2.32	2.29
CO_2	547.2	522.6	509.5	505.8	506.8	509.8	509.2	509.2
Particulate	0.205	0.205	0.186	0.19	0.172	0.174	0.176	0.181
BSFC (Lb./Bhp-hr.)	0.384	0.367	0.358	0.355	0.356	0.358	0.358	0.358
Work (Bhp-hr.)	22.154	22.182	22.244	22.278	22.245	22.191	22.212	22.194

Table A3-cont. Emission Test Results with Cummins L10 Engine using Reformulated Diesel Blend

Test Date	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96	12/19/96
Test Number	354CS	354H1	354H2	354H3	354H4	354H5	354H6	354H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	4.81	4.53	4.63	4.67	4.57	4.6	4.66	4.67
THC	0.45	0.48	0.48	0.5	0.53	0.51	0.49	0.49
CO	2.3	2.17	2.29	2.27	2.27	2.31	2.31	2.33
CO_2	546.4	517	513.8	512.6	509.2	509.6	512.1	512.1
Particulate	0.198	0.198	0.194	0.183	0.185	0.185	0.174	0.163
BSFC (Lb./Bhp-hr.)	0.383	0.363	0.361	0.36	0.358	0.358	0.36	0.36
Work (Bhp-hr.)	22.182	22.278	22.208	22.19	22.264	22.201	22.231	22.202

Test Date	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96	12/20/96
Test Number	355CS	355H1	355H2	355H3	355H4	355H5	355H6	355H7
Cycle Type	Cold	Hot 1	Hot 2	Hot 3	Hot 4	Hot 5	Hot 6	Hot 7
Emissions (g/Bhp-hr.)								
NO_X	4.88	4.63	4.59	4.54	4.59	4.62	4.62	4.58
THC	0.46	0.47	0.5	0.48	0.49	0.48	0.48	0.5
CO	2.25	2.3	2.27	2.24	2.34	2.29	2.32	2.33
CO_2	550.9	519.1	515.6	509.9	510.2	511	511.2	504
Particulate	0.208	0.192	0.183	0.171	0.175	0.177	0.177	0.173
BSFC (Lb./Bhp-hr.)	0.387	0.364	0.362	0.358	0.358	0.359	0.359	0.354
Work (Bhp-hr.)	22.132	22.23	22.243	22.165	22.11	22.111	22.098	22.131

Table A4. Ion and Carbon Analysis Results of Particulate
Pre-1993

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	-	-	0.01	0.01
Nitrate	0.07	0.08	0.08	0.01
Sulfate	**1.10**	0.97	**1.11**	0.09
Ammonium	**0.59**	0.19	**0.58**	0.12
Organic Carbon	**89.00**	9.02	**66.51**	8.57
Elemental Carbon	**133.98**	4.24	**125.87**	7.96
Total Carbon	**222.99**	11.39	**192.39**	15.58
Sum of species	**224.68**	11.34	**194.14**	15.63

Low Aromatic

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	0.01	0.02	0.04	0.03
Nitrate	**0.37**	0.04	**0.39**	0.05
Sulfate	**0.39**	0.10	0.10	0.02
Ammonium	**0.37**	0.04	**0.30**	0.05
Organic Carbon	**56.28**	1.73	**51.29**	3.33
Elemental Carbon	**109.86**	7.98	**118.87**	6.54
Total Carbon	**166.15**	8.55	**170.16**	8.53
Sum of species	**167.28**	8.44	**170.99**	8.49

Reformulated Diesel

	Cold Start Cycle		Hot Start Cycle	
	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*	Emission Rate *mg/Bhp-hr*	SDEV *mg/Bhp-hr*
Chloride	0.03	0.03	0.07	0.11
Nitrate	**0.19**	0.07	**0.17**	0.04
Sulfate	**1.05**	0.81	**0.43**	0.04
Ammonium	**0.43**	0.20	**0.34**	0.05
Organic Carbon	**58.27**	5.83	**51.24**	7.06
Elemental Carbon	**113.87**	18.75	**103.70**	14.82
Total Carbon	**172.15**	23.40	**154.94**	19.49
Sum of species	**173.84**	24.49	**155.94**	19.50

Bold values indicate rates > 2 (analytical uncertainty)

Table A5. Elemental Analysis Results of Particulate

	Pre - 1993				Low Aromatic				Reformulated Diesel				
	Cold Start		Hot Start		Cold Start		Hot Start		Cold Start		Hot Start		
	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	Emission Rate ug/Bhp-hr	SDEV ug/Bhp-hr	
Na	2.45	4.24	19.83	38.07	-	-	-	-	-	-	10.55	11.80	Na
Mg	80.73	43.84	65.69	33.56	79.80	48.63	38.95	11.80	77.01	46.04	50.58	41.45	Mg
Al	3.00	3.19	20.44	18.43	9.42	16.32	2.83	4.15	0.17	0.29	4.13	3.86	Al
Si	619.16	108.92	748.36	91.55	674.07	81.06	635.53	81.27	627.85	185.38	511.81	88.08	Si
P	78.77	16.65	44.32	10.79	89.12	17.69	59.62	12.60	109.81	56.23	71.51	18.35	P
S	1,725.44	186.94	1,349.44	60.45	529.94	68.16	263.78	34.04	924.93	327.38	569.87	32.66	S
Cl	21.87	0.94	26.35	25.01	47.92	11.58	38.94	4.27	28.32	12.60	32.80	10.06	Cl
K	15.17	13.60	13.92	12.32	1.31	2.27	2.16	3.57	7.08	6.36	3.41	3.62	K
Ca	83.86	45.85	79.32	45.69	63.51	13.17	30.41	7.53	94.95	66.33	45.46	11.30	Ca
Ti	1.26	2.19	1.72	3.27	-	-	-	-	-	-	-	-	Ti
V	-	-	0.13	0.32	-	-	-	-	-	-	-	-	V
Cr	0.81	1.38	0.72	1.05	-	-	0.06	0.15	-	-	0.03	0.06	Cr
Mn	1.04	1.43	0.36	0.88	1.39	1.54	0.02	0.05	1.37	2.37	-	-	Mn
Fe	451.36	336.13	212.66	134.66	441.41	41.07	67.22	24.35	330.50	310.58	89.23	25.90	Fe
Co	-	-	0.06	0.12	-	-	-	-	-	-	0.18	0.30	Co
Ni	2.23	3.12	1.34	2.32	-	-	-	-	2.96	2.63	1.11	0.89	Ni
Cu	11.64	6.20	8.46	12.69	6.22	1.43	0.33	0.54	8.57	5.47	4.54	4.39	Cu
Zn	156.07	32.44	95.87	18.77	174.19	41.68	106.55	13.41	267.49	136.00	152.52	19.12	Zn
Ga	-	-	-	-	-	-	-	-	-	-	-	-	Ga
As	-	-	0.08	0.21	-	-	-	-	-	-	0.08	0.19	As
Se	-	-	-	-	-	-	-	-	-	-	-	-	Se
Br	0.30	0.37	0.43	0.50	0.42	0.50	0.35	0.29	0.70	0.58	0.37	0.44	Br
Rb	-	-	-	-	-	-	0.08	0.13	0.08	0.13	0.01	0.02	Rb
Sr	0.61	1.05	0.56	0.74	0.23	0.40	0.02	0.04	0.49	0.43	0.08	0.11	Sr
Y	-	-	-	-	-	-	-	-	-	-	-	-	Y
Zr	-	-	0.73	1.79	-	-	0.00	0.01	0.42	0.73	-	-	Zr
Mo	-	-	-	-	-	-	-	-	-	-	-	-	Mo
Pd	-	-	0.34	0.62	-	-	0.66	1.62	-	-	-	-	Pd
Ag	1.31	2.26	6.24	6.08	0.96	1.35	8.55	14.16	2.76	2.39	3.41	5.11	Ag
Cd	1.28	2.22	2.42	2.52	2.89	2.55	2.76	3.86	1.66	2.77	1.88	2.65	Cd
In	-	-	1.09	2.16	2.45	4.24	2.61	2.65	3.60	6.23	1.25	1.40	In
SN	-	-	1.01	1.26	5.04	8.73	6.86	9.03	6.33	4.73	2.98	4.20	SN
Sb	0.90	1.55	-	-	-	-	3.72	3.29	0.16	0.28	4.64	6.93	Sb
Ba	-	-	4.59	11.24	25.23	33.91	9.63	23.59	2.85	4.94	18.51	22.23	Ba
La	2.62	4.53	12.22	17.68	33.67	26.53	27.28	47.85	9.30	16.10	18.38	22.72	La
Au	-	-	-	-	-	-	-	-	-	-	-	-	Au
Hg	-	-	-	-	-	-	-	-	-	-	-	-	Hg
Tl	-	-	-	-	-	-	-	-	-	-	-	-	Tl
Pb	-	-	0.31	0.77	-	-	-	-	-	-	0.01	0.02	Pb
Ur	-	-	-	-	-	-	0.10	0.18	0.17	0.29	0.00	0.01	Ur
Sum	3,261.86	750.87	2,719.02	332.05	2,189.19	186.65	1,309.03	136.33	2,509.51	1,150.13	1,599.30	144.91	Sum

Bold values indicate measured rates > 2 (analytical uncertainty)

Table A6. Emission Rates of Carbonyls

Pre-1993

	Cold Start Cycle		Hot Start Cycle		Weighted Total(1)	
	Average	SDEV	Average	SDEV	Mean	SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
Formaldehyde	62.33	1.37	56.26	0.95	57.12	0.84
Acetaldehyde	20.23	0.31	17.81	0.20	18.15	0.18
Acrolein	2.18	1.12	2.13	0.74	2.14	0.65
Acetone	7.66	0.02	5.90	0.69	6.15	0.59
Propionaldehyde	4.45	0.08	3.56	0.43	3.69	0.37
Crotonaldehyde	1.32	0.50	1.39	0.28	1.38	0.25
Methacrolein	0.00	0.00	0.00	0.00	0.00	0.00
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00	0.00	0.00
Butyraldehyde	4.72	1.21	4.52	1.12	4.55	0.98
Benzaldehyde	1.23	0.75	1.53	0.42	1.49	0.38
Valeraldehyde	0.50	0.05	0.42	0.03	0.43	0.03
Tolualdehyde	2.84	1.50	3.74	0.96	3.61	0.85
Hexadehyde	0.54	0.10	0.39	0.06	0.41	0.05

Low Aromatic

	Cold Start Cycle		Hot Start Cycle		Weighted Total(1)	
	Average	SDEV	Average	SDEV	Mean	SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
Formaldehyde	54.75	2.10	59.42	5.77	58.75	4.95
Acetaldehyde	17.66	0.45	19.34	1.72	19.10	1.48
Acrolein	5.49	0.69	5.84	0.91	5.79	0.79
Acetone	6.23	0.65	6.81	0.66	6.73	0.57
Propionaldehyde	3.90	0.22	3.92	0.49	3.92	0.42
Crotonaldehyde	2.09	0.34	2.55	0.37	2.48	0.32
Methacrolein	0.10	0.09	0.32	0.44	0.29	0.38
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00	0.00	0.00
Butyraldehyde	1.85	1.02	3.86	1.96	3.57	1.69
Benzaldehyde	2.82	0.36	2.03	1.40	2.14	1.20
Valeraldehyde	0.87	0.23	0.78	0.21	0.79	0.18
Tolualdehyde	2.35	0.58	3.05	0.61	2.95	0.53
Hexadehyde	0.47	0.06	0.45	0.26	0.45	0.22

Reformulated Diesel

	Cold Start Cycle		Hot Start Cycle		Weighted Total(1)	
	Average	SDEV	Average	SDEV	Mean	SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
Formaldehyde	59.69	2.71	59.85	1.00	59.83	0.94
Acetaldehyde	20.10	1.10	19.90	0.58	19.93	0.52
Acrolein	2.52	0.44	2.41	1.71	2.43	1.47
Acetone	6.29	1.39	5.67	0.75	5.76	0.67
Propionaldehyde	4.28	0.84	4.11	0.47	4.13	0.42
Crotonaldehyde	1.46	0.29	1.47	0.47	1.47	0.40
Methacrolein	0.00	0.00	0.14	0.34	0.12	0.29
Methyl Ethyl Ketone	0.00	0.00	0.00	0.00	0.00	0.00
Butyraldehyde	5.21	0.54	4.30	1.07	4.43	0.92
Benzaldehyde	1.32	0.39	1.49	0.64	1.47	0.55
Valeraldehyde	1.28	0.21	1.04	0.24	1.07	0.21
Tolualdehyde	4.12	1.27	4.20	1.06	4.19	0.93
Hexadehyde	0.69	0.04	0.62	0.07	0.63	0.06

(1) Wt. Tot.=(1/7 mg(cold) + 6/7 mg(hot))/1/7 bhp-hr(hot)); SDEV = ((1/6 SDEV(cold)2+(6/7 SDEV(hot))2)^(1/2)

Table A7. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*	Cold Start Cycle Average *mg/bhp-hr*	Cold Start Cycle SDEV *mg/bhp-hr*	Hot Start Cycle Average *mg/bhp-hr*	Hot Start Cycle SDEV *mg/bhp-hr*
Methane	18.23	7.66	14.66	2.47	20.99	5.46	18.17	6.15	22.64	0.36	13.00	5.67
Ethane	0.76	0.26	0.75	0.17	0.70	0.02	0.81	0.08	0.99	0.21	0.74	0.12
Propane	0.14	0.25	0.12	0.18	0.14	0.12	0.07	0.08	0.25	0.03	0.10	0.12
Butane	0.03	0.05	0.03	0.06	0.05	0.09	0.01	0.02	0.00	0.00	0.06	0.10
Pentane	0.00	0.00	0.00	0.01	0.08	0.14	0.04	0.07	0.00	0.00	0.01	0.01
Hexane	3.69	0.33	3.29	0.55	0.60	0.27	0.85	0.12	0.00	0.00	0.10	0.25
Heptane	0.38	0.65	0.42	0.79	1.00	0.41	0.79	0.37	0.00	0.00	0.14	0.35
Octane	1.05	0.11	1.10	0.08	1.35	0.14	1.57	0.21	0.78	0.09	0.76	0.33
Nonane	0.82	0.03	0.78	0.05	0.72	0.09	0.68	0.07	0.62	0.14	0.56	0.39
Decane	1.04	0.12	1.07	0.17	0.83	0.06	0.92	0.09	0.92	0.03	1.17	0.62
Undecane	2.14	0.36	2.73	0.33	1.47	0.04	1.48	0.21	1.56	0.13	1.87	0.31
Dodecane	1.54	0.28	3.92	1.38	2.18	0.60	2.05	0.30	1.14	1.01	1.99	0.81
2-Methylpropane	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.28	0.42	0.41	0.54	0.61
2,2-Dimethylpropane	0.54	0.02	0.42	0.14	0.41	0.08	0.30	0.17	0.55	0.18	0.43	0.23
2-Methylbutane	0.03	0.05	0.00	0.00	0.03	0.06	0.03	0.06	0.00	0.00	0.03	0.04
2,2-Dimethylbutane	1.09	0.16	1.13	0.37	0.56	0.17	0.68	0.39	0.69	0.13	0.65	0.56
2,3-Dimethylbutane	0.00	0.00	0.00	0.00	0.68	0.15	0.19	0.30	0.00	0.00	0.00	0.00
2-Methylpentane	2.62	0.90	2.01	1.04	3.72	2.00	4.01	2.04	1.25	2.16	2.58	2.05
3-Methylpentane	1.00	0.08	1.27	0.38	0.69	0.36	0.38	0.23	0.91	0.28	0.87	0.39
2,2,3-Trimethylbutane	0.17	0.29	0.00	0.00	0.23	0.39	0.09	0.22	0.00	0.00	0.00	0.00
2,2-Dimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylpentane	0.83	0.36	0.91	0.15	1.06	0.49	1.16	0.44	0.95	0.12	0.88	0.46
2,4-Dimethylpentane	0.00	0.00	0.00	0.00	0.15	0.25	0.17	0.27	0.00	0.00	0.00	0.00
3,3-Dimethylpentane	0.33	0.29	0.27	0.30	0.49	0.04	0.61	0.11	0.40	0.36	0.43	0.22
2-Methylhexane	0.14	0.24	0.17	0.26	0.76	0.70	0.49	0.56	0.30	0.26	0.36	0.29
3-Methylhexane	1.23	0.31	1.05	0.23	1.42	0.21	1.35	0.23	1.25	0.05	1.05	0.15
2,2,4-Trimethylpentane (i-Octane)	0.00	0.00	0.13	0.33	0.29	0.51	0.11	0.24	0.15	0.26	0.00	0.00
2,3,3-Trimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4-Trimethylpentane	0.00	0.00	0.23	0.25	0.21	0.36	0.00	0.00	0.36	0.62	0.15	0.36
3-Ethylpentane	0.00	0.00	0.10	0.25	0.72	0.07	0.68	0.37	0.00	0.00	0.00	0.00
2,2-Dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.66	0.27	0.43
2,3-Dimethylhexane	0.22	0.38	0.00	0.00	0.00	0.00	0.45	0.38	0.18	0.31	0.24	0.40
2,4-Dimethylhexane	0.17	0.30	0.00	0.00	0.00	0.00	0.19	0.30	0.00	0.00	0.00	0.00
2,5-Dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.24	0.00	0.00	0.00	0.00
3,3-Dimethylhexane	0.00	0.00	0.08	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A7. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
2-Methylheptane	0.00	0.00	0.10	0.24	0.47	0.43	0.37	0.30	0.00	0.00	0.00	0.00
3-Methylheptane	0.00	0.00	0.00	0.00	0.36	0.33	0.27	0.30	0.00	0.00	0.00	0.00
4-Methylheptane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylheptane	0.00	0.00	0.00	0.00	0.68	0.10	0.70	0.10	0.30	0.53	0.16	0.38
2,4-Dimethylheptane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,5-Dimethylheptane	2.03	0.45	2.51	0.66	2.25	1.45	0.94	0.91	1.08	1.87	0.49	0.78
2,2,5-Trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,5-Trimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyloctane	0.00	0.00	0.00	0.00	0.64	0.11	0.67	0.11	0.00	0.00	0.00	0.00
3-Methyloctane	1.21	0.10	1.34	0.28	0.87	0.09	1.13	0.16	1.59	0.62	1.59	0.29
2,2-Dimethyloctane	0.00	0.00	0.33	0.38	0.45	0.39	0.24	0.39	0.00	0.00	0.19	0.46
2,4-Dimethyloctane	1.96	0.36	1.94	0.41	1.24	0.09	1.30	0.17	2.21	0.18	2.29	0.41
Cyclopentane	0.72	0.12	0.66	0.18	1.16	0.10	1.04	0.19	0.57	0.08	0.48	0.28
Methylcyclopentane	0.22	0.38	0.10	0.25	0.75	0.44	0.37	0.20	0.23	0.40	0.19	0.30
Cyclohexane	1.05	0.23	1.00	0.14	1.38	0.45	1.79	0.23	0.93	0.23	1.20	0.18
t-1,2-Dimethylcyclopentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-1,3-Dimethylcyclopentane	0.00	0.00	0.00	0.00	0.55	0.14	0.47	0.25	0.00	0.00	0.00	0.00
Methylcyclohexane	0.87	0.40	0.96	0.32	1.82	0.05	2.35	0.31	0.42	0.38	0.49	0.39
1c,2t,3-Trimethylcyclopentane	1.35	0.06	0.90	0.29	0.18	0.30	0.09	0.23	1.05	0.43	1.16	0.34
c-1,2-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.14	0.25	0.31	0.48	0.00	0.00	0.00	0.00
c-1,3-Dimethylcyclohexane	0.00	0.00	0.00	0.00	1.45	0.55	1.49	0.42	0.00	0.00	0.00	0.00
t-1,3-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.83	0.06	1.30	0.30	0.00	0.00	0.00	0.00
t-1,4-Dimethylcyclohexane	0.00	0.00	0.00	0.00	0.15	0.27	0.17	0.26	0.00	0.00	0.00	0.00
Ethylcyclohexane	0.00	0.00	0.07	0.18	0.54	0.51	4.42	4.94	12.98	11.28	9.34	7.58
Ethene	28.54	0.70	25.93	1.13	25.58	0.90	28.09	0.99	27.39	0.47	26.52	0.94
Propene	11.01	0.28	10.20	0.37	9.41	1.43	9.90	0.30	9.55	0.40	9.68	0.16
1-Butene	2.85	0.11	2.55	0.17	2.40	0.13	2.64	0.07	2.85	0.09	2.77	0.13
c-2-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.53
t-2-Butene	0.64	0.03	0.60	0.08	0.55	0.09	0.61	0.07	0.41	0.36	0.49	0.24
2-Methylpropene	1.92	0.18	1.98	0.30	1.54	0.13	1.69	0.33	1.95	0.20	1.94	0.30
1-Pentene	1.25	0.27	1.27	0.37	1.13	0.10	1.17	0.21	1.04	0.07	1.29	0.40
c-2-Pentene	0.64	0.78	0.37	0.30	0.37	0.65	0.49	0.78	0.00	0.00	0.08	0.20
t-2-Pentene	0.21	0.36	0.32	0.26	0.00	0.00	0.16	0.25	0.31	0.27	0.11	0.27
2-Methyl-1-Butene	0.97	0.21	0.87	0.32	0.97	0.10	0.81	0.13	0.75	0.07	0.79	0.10

Table A7. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
3-Methyl-1-Butene	0.80	0.07	0.75	0.07	0.78	0.36	0.35	0.28	0.54	0.10	0.33	0.26
2-Methyl-2-Butene	0.25	0.44	0.21	0.32	0.62	0.14	0.34	0.22	0.14	0.24	0.00	0.00
1-Hexene	1.24	0.22	1.25	0.16	1.26	0.42	1.12	0.26	1.50	0.28	1.16	0.15
c-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-3-Hexene	0.00	0.00	0.07	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-3-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-1-Pentene	1.13	0.15	0.83	0.19	0.74	0.11	0.85	0.19	0.79	0.13	0.66	0.51
4-Methyl-1-Pentene	1.32	0.11	1.25	0.25	1.19	0.15	1.27	0.20	1.10	0.14	1.12	0.20
2-Methyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-c-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.23	0.22	0.39	0.18	0.44
3-Methyl-t-2-Pentene	0.16	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-c-2-Pentene	0.00	0.00	0.94	1.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-t-2-Pentene	1.89	1.62	1.25	0.47	2.45	2.09	1.97	2.57	2.40	1.73	1.26	1.96
3,3-Dimethyl-1-Butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Heptene	1.06	0.15	0.90	0.47	1.30	0.26	1.45	0.28	1.13	0.18	1.09	0.27
c-2-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-3-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4-Dimethyl-1-Pentene	0.16	0.27	0.00	0.00	0.00	0.00	0.09	0.23	0.00	0.00	0.00	0.00
3-Methyl-1-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methyl-t-3-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Octene	0.71	0.09	0.71	0.22	0.86	0.09	0.92	0.09	0.48	0.42	0.74	0.09
c-2-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-2-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
t-4-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,4,4-Trimethyl-1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,4,4-Trimethyl-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Ethyl-c-2-Pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Nonene	0.75	0.16	0.55	0.07	1.12	0.24	1.27	0.13	0.77	0.04	0.76	0.20
Propadiene	0.19	0.11	0.03	0.06	0.00	0.00	0.00	0.01	0.03	0.06	0.04	0.04
1,3-Butadiene	2.08	0.52	1.75	0.11	2.19	0.53	2.50	0.13	1.72	0.04	1.87	0.15
2-Methyl-1,3-Butadiene	0.74	0.17	0.85	0.23	0.68	0.59	1.09	0.25	0.69	0.22	0.81	0.41
Cyclopentadiene	0.00	0.00	0.05	0.12	0.52	0.09	0.51	0.32	0.00	0.00	0.00	0.00
Cyclopentene	0.35	0.30	0.50	0.47	0.38	0.33	0.22	0.25	0.00	0.00	0.00	0.00

Table A7. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
1-Methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methylcyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyclohexene	0.00	0.00	0.09	0.23	0.36	0.33	0.24	0.39	0.00	0.00	0.00	0.00
Ethyne	7.93	1.01	6.67	0.55	6.81	0.46	6.17	0.56	6.74	0.24	5.48	0.55
Propyne	0.00	0.00	0.06	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butyne	0.00	0.00	0.32	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Butyne	1.56	0.21	1.65	1.24	1.65	0.72	1.31	1.20	0.47	0.81	0.19	0.47
Benzene	6.49	0.04	5.80	0.30	7.29	0.38	8.15	1.17	6.78	0.19	5.65	0.80
Toluene	2.17	0.10	1.89	0.27	1.96	0.23	2.31	0.33	1.86	0.55	1.86	0.25
Ethylbenzene	0.74	0.06	1.30	0.66	0.54	0.11	0.69	0.20	1.03	0.65	1.20	0.72
o-Xylene	0.85	0.09	0.77	0.09	0.58	0.05	0.62	0.11	0.99	0.11	0.86	0.24
m&p-Xylene	1.90	0.23	2.12	0.55	1.24	0.20	1.24	0.34	1.84	0.39	2.19	0.36
n-Propylbenzene	0.77	0.19	0.25	0.28	0.18	0.30	0.24	0.26	0.16	0.28	0.57	0.34
i-Propylbenzene	0.25	0.43	0.00	0.00	0.96	0.07	0.91	0.10	0.00	0.00	0.00	0.00
1-Methyl-2-ethylbenzene	0.68	0.10	0.79	0.29	0.15	0.26	0.26	0.29	0.57	0.98	0.78	1.00
1-Methyl-3-ethylbenzene	1.22	0.05	1.23	0.12	0.37	0.64	0.57	0.48	1.62	0.33	1.47	0.19
1-Methyl-4-ethylbenzene	0.81	0.09	0.75	0.09	0.00	0.00	0.09	0.22	0.92	0.21	0.88	0.16
1,2-Dimethyl-3-ethylbenzene	0.45	0.48	0.20	0.32	0.14	0.24	0.11	0.27	0.00	0.00	0.00	0.00
1,2-Dimethyl-4-ethylbenzene	0.57	0.51	0.66	0.37	0.00	0.00	0.00	0.00	0.81	0.16	0.74	0.10
1,3-Dimethyl-2-ethylbenzene	0.54	0.01	0.51	0.19	0.28	0.25	0.46	0.26	0.36	0.62	0.57	0.43
1,3-Dimethyl-4-ethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Dimethyl-2-ethylbenzene	0.51	0.12	0.51	0.11	0.62	0.12	0.62	0.10	0.56	0.15	0.61	0.12
1,2,3-Trimethylbenzene	1.37	0.55	1.25	0.54	0.00	0.00	0.00	0.00	0.60	0.14	1.06	0.29
1,2,4-Trimethylbenzene	1.71	0.06	1.76	0.14	1.15	0.29	1.13	0.14	1.90	0.26	2.04	0.18
1,3,5-Trimethylbenzene	0.93	0.13	0.96	0.36	0.19	0.33	0.29	0.32	0.90	0.36	0.96	0.23
Indan	0.16	0.28	0.28	0.46	0.00	0.00	0.00	0.00	0.61	0.12	0.56	0.16
i-Butylbenzene	0.00	0.00	0.10	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
s-Butylbenzene	0.58	0.05	0.73	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methyl-Butylbenzene	0.00	0.00	3.85	5.96	1.84	3.18	2.44	3.78	0.00	0.00	0.00	0.00
tert-1-Butyl-2-Methyl-Benzene	0.91	0.43	0.52	0.49	1.03	0.91	1.01	0.81	0.74	0.32	0.45	0.24
tert-1-Butyl-3,5-Dimethyl-Benzene	1.03	0.19	0.71	0.72	0.19	0.34	0.07	0.17	0.58	0.05	0.58	0.07
1,2-Diethylbenzene	0.00	0.00	0.00	0.00	0.29	0.50	0.15	0.23	0.22	0.38	0.00	0.00
1,3-Diethylbenzene	1.12	0.47	0.79	0.47	0.54	0.08	0.63	0.22	1.03	0.28	0.84	0.22
1,4-Diethylbenzene	0.13	0.23	0.33	0.46	0.00	0.00	0.07	0.17	0.09	0.16	0.00	0.00

Table A7. Emission Rates for Speciated Hydrocarbons.

	Pre - 1993				Low Aromatic				Reformulated Diesel			
	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV	Cold Start Cycle Average	Cold Start Cycle SDEV	Hot Start Cycle Average	Hot Start Cycle SDEV
	mg/bhp-hr	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*	*mg/bhp-hr*
1-Methyl-2-n-Propylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.37	0.64	0.36
1-Methyl-3-n-Propylbenzene	0.57	0.07	0.58	0.61	0.00	0.00	0.00	0.00	1.72	0.35	1.50	0.32
1-Methyl-4-n-Propylbenzene	1.00	0.33	0.81	1.14	0.00	0.00	0.13	0.33	2.34	0.26	2.37	0.39
1-Methyl-2-i-Propylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Methyl-3-i-Propylbenzene	0.76	0.19	0.77	0.39	0.00	0.00	0.23	0.36	0.00	0.00	0.14	0.34
1-Methyl-4-i-Propylbenzene	0.75	0.36	0.99	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,3,4-Tetramethylbenzene	1.11	0.22	1.06	1.15	0.93	1.03	0.83	0.79	1.21	0.07	1.25	0.12
1,2,3,5-Tetramethylbenzene	0.67	0.05	0.84	0.21	0.44	0.76	0.47	0.74	1.07	0.22	1.24	0.13
1,2,4,5-Tetramethylbenzene	11.17	1.35	7.50	5.96	4.85	4.21	5.15	4.07	12.22	4.14	9.98	2.13
n-Pent-Benzene	0.00	0.00	0.68	0.63	0.30	0.52	0.33	0.39	2.17	0.21	2.27	0.23
Styrene	0.97	0.34	1.32	0.31	2.10	1.60	1.49	0.21	1.36	0.19	1.46	0.31
Naphthalene	1.33	0.09	1.75	0.50	1.55	0.54	1.77	0.25	1.18	0.07	1.29	0.25
Methyl-t-Butyl-Ether	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethyl-t-Butyl-Ether	0.00	0.00	3.26	1.27	0.00	0.00	2.72	0.35	0.00	0.00	0.37	0.90
Unknown (C1-C4)	0.42	0.42	0.27	0.34	0.28	0.11	0.31	0.10	0.40	0.13	0.58	0.35
Unknown (C4-C12)	31.42	3.62	37.72	7.17	23.72	0.77	24.35	5.70	38.43	4.21	41.05	8.86
Total	194.04	36.28	196.97	58.24	176.03	47.85	185.21	59.00	207.61	47.64	194.11	56.45

Table A8. Emission Rates for Polycyclic Aromatic Hydrocarbons.

PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3 µg/bhp-hr	338H4,H5 µg/bhp-hr	338H6,H7 µg/bhp-hr	346H5,H6 µg/bhp-hr	347H3,H4 µg/bhp-hr	347H5,H6 µg/bhp-hr	351H3,H4 µg/bhp-hr	352H3,H4 µg/bhp-hr	353H5,H6 µg/bhp-hr
2.3.5-trimethylnaphthalene[a,b]	289.12	278.60	283.31	15.49	12.07	16.74	58.94	56.40	53.31
phenanthrene[c]	332.81	347.09	330.23	152.05	178.86	151.84	173.66	210.89	277.64
anthracene[d]	37.26	39.50	39.92	16.73	20.89	18.01	20.33	24.43	33.72
Me-phenanthrenes/anthracenes[c,e]	313.02	343.10	337.86	26.76	24.70	24.05	90.01	101.44	144.50
fluoranthene[d]	137.03	122.55	125.77	124.29	153.31	119.49	95.31	126.50	147.40
pyrene[d]	210.44	177.60	191.05	195.57	253.81	184.18	163.44	217.87	239.15
benzo[c]phenanthrene	3.26	3.05	2.78	1.65	1.89	1.67	1.31	1.49	1.82
benzo[ghi]fluoranthene[f]	27.93	23.40	23.20	17.14	21.30	18.35	14.61	16.98	19.22
cyclopenta[cd]pyrene	25.71	17.51	21.11	24.04	29.74	24.67	17.99	20.87	24.89
benz[a]anthracene	16.19	14.87	18.19	10.74	11.62	9.34	8.17	12.51	12.19
chrysene + triphenylene[g]	17.14	15.82	19.11	9.94	10.98	10.21	9.08	14.11	13.41
benzo[b+i+k]fluoranthene[g]	30.93	26.95	35.28	21.09	23.37	25.04	20.94	36.76	29.85
benzo[e]pyrene	17.07	13.83	19.22	13.57	16.08	14.00	13.54	24.69	18.73
benzo[a]pyrene	21.39	16.82	23.15	14.90	18.02	16.53	14.59	26.05	21.14
perylene	4.55	3.35	5.05	2.92	4.38	3.82	2.95	5.25	4.36
indeno[1,2,3-cd]fluoranthene	0.41	0.33	0.28	0.24	0.19	0.22	0.17	0.17	0.17
benzo[c]chrysene	0.28	0.24	0.34	0.21	0.13	0.22	0.11	0.13	0.19
dibenz[a,j]anthracene	0.89	0.99	0.92	0.65	0.45	0.56	0.57	0.69	0.75
indeno[1,2,3-cd]pyrene	19.99	16.51	21.84	16.23	12.33	13.57	14.26	32.12	20.10
dibenz[a,h + a,c]anthracene[g]	1.53	1.40	1.70	0.94	0.73	0.93	0.90	2.22	1.34
benzo[b]chrysene	0.39	0.41	0.39	0.21	0.13	0.12	0.22	0.28	0.32
benzo[ghi]perylene	50.47	38.97	58.09	48.15	35.51	35.77	39.09	90.44	52.70
coronene	13.04	8.33	7.10	5.04	4.42	5.33	5.98	9.14	7.32
dibenzo[a,l]pyrene	3.28	2.84	2.39	1.42	1.24	1.11	1.81	2.35	2.77
dibenzo[a,e]pyrene	1.40	1.08	0.83	0.68	0.60	0.56	0.96	1.25	1.19
dibenzo[a,i]pyrene	1.14	0.85	0.73	0.18	0.34	0.31	0.55	0.76	0.83
dibenzo[a,h]pyrene	1.62	1.22	1.15	0.83	0.75	0.68	0.61	0.91	1.00

Table A8-cont. Emission Rates for Polycyclic Aromatic Hydrocarbons (cont.).

[a] Lower limit based on summing amounts on front PUF and back PUF (amount on filter negligible).
[b] The area of the molecular ion peak (m/z 170) and the response factor for 2,3,5-trimethylnaphthalene relative to deuterated phenanthrene were used to quantify 2,3,5-trimethylnaphthalene and a co-eluting isomer.

[c] Sum of amounts on filter, front PUF and back PUF.
[d] Sum of amounts on filter and front PUF; negligible amount found on back PUF.
[e] The areas of the molecular ion of the five isomers present were summed and the response factor for 1-methylphenanthrene relative to deuterated phenanthrene was used to quantify all isomers.
[f] Standard not available, response factor for cyclopenta[cd]pyrene relative to deuterated chrysene used for quantification.
[g] Co-eluting isomers.

Table A9. Emission Rates for Nitro-Polycyclic Aromatic Hydrocarbons.

Nitro-PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3 µg/bhp-hr	338H4,H5 µg/bhp-hr	338H6,H7 µg/bhp-hr	346H5,H6 µg/bhp-hr	347H3,H4 µg/bhp-hr	347H5,H6 µg/bhp-hr	351H3,H4 µg/bhp-hr	352H3,H4 µg/bhp-hr	353H5,H6 µg/bhp-hr
1-nitronaphthalene	0.53	0.53	0.50	0.34	0.31	0.31	0.44	0.48	1.07
2-nitronaphthalene	1.50	1.53	1.51	0.64	0.68	0.74	1.13	1.17	1.80
methylnitronaphthalenes	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
4-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
5-nitroacenaphthene	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrofluorene	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
9-nitroanthracene[a]	0.56	0.62	0.50	0.56	0.54	0.53	0.30	0.28	0.44
1-nitropyrene	2.10	2.13	1.64	2.00	2.20	2.01	1.23	2.08	1.61
3-nitrofluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
4-nitropyrene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
7-nitrobenz[a]anthracene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrochrysene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrobenzo[a]pyrene	0.32	0.39	0.22	0.47	0.41	0.39	0.31	0.45	0.43

[a]For the Pre-1993 Fuel and the Reformulated Blend, interferences prevented quantification using the molecular ion at m/z 223 and the $[M-NO]^+$ fragment ion was used.

ATTACHMENT B

QUALITY CONTROL / QUALITY ASSURANCE REPORT

QUALITY CONTROL / QUALITY ASSURANCE REPORT

This chapter discusses QA/QC activities and results as described in the QA Project Plan (Norbeck et al, 1996). Please see that document for additional information on QA/QC procedures and goals.

Section 1.1 of this chapter presents Data Quality Goals and Data Quality Results. The types of QC data collected during the study are described in Section 1.2. The quantitative QC data are shown in Section 1.3. Section 1.4 describes variability in replicate tests and compares this variability to QC results. Section 1.5 summarizes data quality achieved with data quality goals and discuses the adequacy of the data set for its intended use.

1 Data Quality Goals and Results

1.1 Primary Goals and Results

Goals were to collect at least 2 valid samples from each fuel/cycle combination. Criteria for validity of samples were: conformity of the dynamometer load test cycle with requirements specified in the Code of Federal Regulations (CFR); conformity of analytical procedures and QC check tolerances with requirements specified in the CFR for criteria gases and total particulates; comparability of sampling procedures and sampling performance with industry standards for various speciated measurements. The number of valid samples collected is shown in Table 1-1. All primary goals were met.

Table 1-1 Primary Goals

Fuel:	Pre 93		Reformulated		Low Aromatic	
Cycle:	Cold	Hot	Cold	Hot	Cold	Hot
Criteria gases	7	38	5	34	3	20
Speciated HC	3	6	3	6	3	6
Oxygenates	2	5	3	6	3	7
Mass	7	38	5	34	3	20
Ions	3	7	3	6	3	6
EC/OC	3	7	3	6	3	6
Elements	3	7	3	6	3	6
MOUDI	2	4	2	4	3	6

1.2 Supplementary Goals and Results

Supplementary goals were to achieve analytical accuracies and precisions comparable with data from standard emission test protocols and with results from other studies.

The supplementary goals are shown in Table 1-2. The values achieved during the study are shown in Table 1-3.

Table 1-2 Supplemental Data Quality Goals

Species	Accuracy	Precision	Detection Limit
Exhaust Emissions[a]			
Total PM	20%	10%	0.01 g/bhp-hr
THC	35%	15%	0.01 g/bhp-hr
NOx	10%	5%	0.01 g/bhp-hr
CO	35%	20%	0.06 g/bhp-hr
Size Fractionated PM	20%	10%	0.01 g/bhp-hr
Elements	30%	20%	0.003-.130 mg/bhp-hr
Ions	30%	20%	0.124 mg/bhp-hr
Carbon(elem./organic)	30%	20%	0.248 mg/bhp-hr
Chemical Analyses[b]			
C1-C4 Hydrocarbons	10%	20%	0.01 ppm carbon
C4-C12 Hydrocarbons	10%	20%	0.01 ppm carbon
Carbonyls	2%	20%	0.02 ug/ml
Nitrosomopholine	N.D.	±0.014 ug/sample	0.05 ug/sample
Nitro-PAH	N.D.	20%	2-6 ug/sample
PAH	N.D.	20%	2-6 ug/sample
Dioxins			

a-engine testing/sampling/analysis b-analytical N.D.-Not Determined

Table 1-3 Supplemental Data Quality Results

Species	Accuracy	Precision	Detection Limit
Exhaust Emissions[a]			
Total PM	<3%	5.5%	0.002 g/bhp-hr
THC	< 2%	4.0%	0.042 g/bhp-hr
NOx	<2%	1.9%	0.064 g/bhp-hr
CO	<2%	4.7%	0.058 g/bhp-hr
Size Fractionated PM	<1%	<1%	0.002 g/bhp-hr
Elements	%	14% to 111%	0.003 to 0.130 mg/bhp-hr
Ions	%	22% to 55%	0.124 mg/bhp-hr
Carbon(elem./organic)	%	9% / 11%	0.248 mg/bhp-hr
Chemical Analyses[b]			
C1-C4 Hydrocarbons	-0.1% to 2.8%	<1.1%	0.01 ppm carbon
C4-C12 Hydrocarbons	-5.6% to 2.4%	<3.5%	0.01 ppm carbon
Carbonyls	<2.2%	<2.4%	0.02 ug/ml

a-engine testing/sampling/analysis b-analytical N.D.-Not Determined

2 QA/QC Activities

The quality of results for all emissions measurements in this program includes dependence on a common baseline:

conformity of the dynamometer load test cycle with requirements specified in the CFR

adherence to sampling procedures defined in the CFR

the accuracy and precision of the CVS system

correctness of data calculations

completeness of record keeping and data archiving

In addition to these base requirements, the quality of individual measurement types depend on one or more of the following:

accuracy and precision of criteria gas analyzers

accuracy and precision of sample collection flow rates

accuracy and precision of laboratory analyses

For some measurements, the quality of results can also be assessed by comparing data from two methods to provide additional validation.

The QA/QC activities undertaken in each of these areas is summarized below. The results of these activities are given in Section 3.

Dynamometer Loads

The LACMTA dynamometer system includes a test labeled "EPA Heavy Duty Transient Regression Report." This report includes two test pass/fail checks labeled "Regression Analysis" and "Power Validation." These tests were conducted and reviewed for each emission test run.

CVS

The CVS system and mass flow controllers on the secondary dilution tunnel received an external audit by Dick Munns Company on April 27, 1997.

Data Calculations

Equations for calculation of emission rate data from sample concentrations, background concentrations and flow rates, were obtained from the CFR. The results of computer data processing were spot-checked by manual calculation for particle mass and particle species, for speciated hydrocarbons, and for carbonyls.

Data Record Completeness

The raw source data archives consist of three ring binders containing hand-written field data sheets and hard copy printouts of analytical data. The presence of the appropriate data sheets and printouts was checked for each test run.

Criteria Gas Analyzers

The criteria gas analyzers received audits by the ARB on 5/16/96, 5/20/96, 7/11/96, 1/16/97, and 1/23/97. The criteria gas analyzers receive a zero and span check with 2% tolerance for each species before and after each sample bag analysis.

Sample Collection

The mass flow controllers for total particle sampling received an external audit by Dick Munns Company on April 22, 1997.

Flow meters for Teflon filter (elemental analysis) and quartz filter sampling (ions and OC/EC analysis) were calibrated against a NIST traceable dry gas meter at CE-CERT prior to sampling.

The Method 5 sampler for impactor sampling (particle size distribution) includes a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter at CE-CERT prior to sampling.

The carbonyl sampler includes a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter by CE-CERT prior to sampling.

A dilution tunnel particle sampling blank was collected for each fuel type.

Laboratory Analyses

Gravimetric procedures for total mass analyses at LACMTA were conducted in accordance with CFR requirements and tolerances.

Gravimetric analyses at CE-CERT were checked against zero every fifth weighing, against a calibration weight every twentieth weighing, and against reference filters once per weighing session.

Carbonyl analyses were checked each run against control standards.

Speciated hydrocarbon analyses were checked each day against a 23-component control mixture.

Intermethod Comparisons

Total hydrocarbons by FID were compared with the sum of speciated hydrocarbons.

MTA total particle mass was compared with sum of particle species.

Particle sulfur was compared with particle sulfate.

3 QA/QC Data

3.1 Dynamometer load cycles

Dynamometer cycle Regression Analysis and Power Validation test tolerances were met for all tests. The cycle validation test results are archived at CE-CERT. Table 1-4 shows the cycle validation tests results archived at CE-CERT.

3.2 CVS flows

CVS flow system and mass flow controllers for secondary dilution tunnel were calibrated by LACMTA at installation. Results archived at LACMTA.

External audit test results for the CVS flow rate showed LACMTA flow rate within 2% of audit flow rate (Dick Munns Co., 1997).

3.3 Criteria gas analyzers THC, CO, NOx, CO_2

Adherence to CFR procedures

The LACMTA operates a dedicated emissions testing facility designed specifically to operate in conformance with CFR requirements.

Calibrations

Six-point calibrations were performed on the THC, CO, NOx, and CO_2 analyzers by LACMTA on November 24, 1996 and January 6, 1997. Results were within requirements as specified in CFR 1321-24. Records are archived at LACMTA.

QC Checks

Zero and span checks were conducted before and after each bag analysis for every test cycle. On three occasions NOx zero checks slightly exceeded tolerances, being 2% to 5% of full-scale. Otherwise all post analytical zero and span checks met the 2% or less drift limit as required in CFR 86.1340. Table 1-4 shows the status of zero and span QC checks. QC check printouts for the first four runs and a scattered few other runs are missing.

Table 1-4 Validation Results for MTA Cycle and Criteria Gases

Test Date	Test Time	Fuel Type	Test Code	data sheets present	CO2 span corr. made	zero	span	regr	power
12/2/96	8:00	Pre-93							
12/2/96	12:10:19	Pre-93	337CS	yes		b	b	ok	ok
12/2/96	12:10:19	Pre-93	337H1	yes		b	b	ok	ok
12/2/96	13:46:37	Pre-93	337H2	yes		b	b	ok	ok
12/2/96	14:30:00	Pre-93	337H3	no		b	b	ok	ok
12/3/96	7:10:47	Pre-93	338CS	yes		ok	ok	ok	ok
12/3/96	7:10:47	Pre-93	338H1	yes		ok	ok	ok	ok
12/3/96	8:46:13	Pre-93	338H2	yes		ok	ok	ok	ok
12/3/96	9:26:09	Pre-93	338H3	yes		ok	ok	ok	ok

12/3/96	10:17:43	Pre-93	338H4	yes		ok	ok	ok	ok
12/3/96	10:57:11	Pre-93	338H5	yes		ok	ok	ok	ok
12/3/96	11:46:36	Pre-93	338H6	yes		ok	ok	ok	ok
12/3/96	12:29:51	Pre-93	338H7	yes		ok	ok	ok	ok
12/3/96	13:16:28	Pre-93	338H8	yes		ok	ok	ok	ok
12/3/96	13:57:08	Pre-93	338H9	yes		ok	ok	ok	ok
12/4/96	7:25:21	Pre-93	339CS	yes		ok	NOx	ok	ok
12/4/96	7:25:21	Pre-93	339H1	yes		ok	NOx	ok	ok
12/4/96	8:58:04	Pre-93	339H2	yes		ok	NOx	ok	ok
12/4/96	9:44:22	Pre-93	339H3	yes		ok	ok	ok	ok
12/4/96	10:34:34	Pre-93	339H4	yes		ok	ok	ok	ok
12/4/96	11:20:47	Pre-93	339H5	yes		ok	ok	ok	ok
12/4/96	13:05:02	Pre-93	339H6	yes		ok	ok	ok	ok
12/4/96	13:50:31	Pre-93	339H7	yes		ok	ok	ok	ok
12/5/96	7:31:33	Pre-93	340CS	yes		ok	ok	ok	ok
12/5/96	7:31:33	Pre-93	340H1	yes		ok	ok	ok	ok
12/5/96	9:12:47	Pre-93	340H2	yes		ok	ok	ok	ok
12/5/96	9:52:18	Pre-93	340H3	yes		ok	ok	ok	ok
12/5/96	10:36:21	Pre-93	340H4	yes		ok	ok	ok	ok
12/6/96	12:54:33	Pre-93	341CS	yes		ok	ok	ok	ok
12/6/96	12:54:33	Pre-93	341H1	yes		ok	ok	ok	ok
12/6/96	14:28:25	Pre-93	341H2	yes		ok	ok	ok	ok
12/6/96	15:18:36	Pre-93	341H3	a		ok	ok	ok	ok
12/9/96	9:33:00	LowArom	344header						
12/9/96	13:47:24	LowArom	344H1	yes		ok	ok	ok	ok
12/9/96	14:44:28	LowArom	344H2	yes		ok	ok	ok	ok
12/9/96	15:32:18	LowArom	344H3	yes		ok	ok	ok	ok
12/9/96	16:14:19	LowArom	344H4	yes		ok	ok	ok	ok
12/10/96	8:00	LowArom	345tunnel						
12/10/96	10:39:21	LowArom	345CS	yes		ok	ok	ok	ok
12/10/96	10:39:21	LowArom	345H1	yes		ok	ok	ok	ok
12/10/96	12:21:25	LowArom	345H2	yes		ok	ok	ok	ok
12/10/96	13:10:54	LowArom	345H3	yes		ok	ok	ok	ok
12/10/96	13:56:45	LowArom	345H4	yes		ok	ok	ok	ok
12/11/96	7:32:18	LowArom	346CS	yes		ok	ok	ok	ok
12/11/96	7:32:18	LowArom	346H1	yes		ok	ok	ok	ok
12/11/96	9:03:43	LowArom	346H2	yes		ok	ok	ok	ok
12/11/96	9:48:53	LowArom	346H3	yes		ok	ok	ok	ok
12/11/96	10:34:12	LowArom	346H4	yes		ok	ok	ok	ok
12/11/96	13:25:31	LowArom	346H5	yes		ok	ok	ok	b
12/11/96	14:26:29	LowArom	346H6	yes		ok	ok	ok	ok
12/11/96	15:15:58	LowArom	346H7	yes		ok	ok	ok	ok
12/12/96	7:33:31	LowArom	347CS	yes		ok	ok	ok	ok
12/12/96	7:33:31	LowArom	347H1	yes		ok	ok	ok	ok
12/12/96	9:00:02	LowArom	347H2	yes		ok	ok	ok	ok
12/12/96	10:01:15	LowArom	347H3	yes		ok	ok	ok	ok
12/12/96	10:47:17	LowArom	347H4	yes		ok	ok	ok	ok
12/12/96	12:00:31	LowArom	347H5	yes		ok	ok	ok	ok
12/12/96	13:01:41	LowArom	347H6	yes		ok	ok	ok	ok

12/13/96		Reform	348 header						
12/13/96	13:59:39	Reform	348H1	yes		ok	ok	ok	ok
12/13/96	14:51:32	Reform	348H2	yes		ok	ok	ok	ok
12/16/96	7:00	Reform	351tunnel						
12/16/96	8:19:31	Reform	351CS	yes		ok	ok	ok	ok
12/16/96	8:19:31	Reform	351H1	yes		ok	ok	ok	ok
12/16/96	9:54:11	Reform	351H2	yes		ok	ok	ok	ok
12/16/96	10:52:37	Reform	351H3	yes		ok	ok	ok	ok
12/16/96	11:47:06	Reform	351H4	yes		ok	ok	ok	ok
12/16/96	12:34:18	Reform	351H5	yes		ok	ok	ok	ok
12/16/96	13:16:19	Reform	351H6	yes		ok	ok	ok	ok
12/16/96	14:12:00	Reform	351H7	yes		ok	ok	ok	ok
12/17/96	7:22:39	Reform	352CS	yes		ok	ok	ok	ok
12/17/96	7:22:39	Reform	352H1	yes		ok	ok	ok	ok
12/17/96	8:53:01	Reform	352H2	yes		ok	ok	ok	ok
12/17/96	9:39:23	Reform	352H3	yes		ok	ok	ok	ok
12/17/96	10:35:04	Reform	352H4	yes		b	ok	ok	ok
12/17/96	11:27:06	Reform	352H5	yes		ok	ok	ok	ok
12/17/96	12:09:43	Reform	352H6	yes		ok	ok	ok	ok
12/17/96	12:51:34	Reform	352H7	yes		ok	ok	ok	ok
12/18/96	7:25:42	Reform	353CS	yes		ok	ok	ok	ok
12/18/96	7:25:42	Reform	353H1	yes		ok	ok	ok	ok
12/18/96	8:55:44	Reform	353H2	yes		ok	ok	ok	ok
12/18/96	9:53:58	Reform	353H3	yes		ok	ok	ok	ok
12/18/96	10:34:41	Reform	353H4	yes		ok	ok	ok	ok
12/18/96	11:29:25	Reform	353H5	yes		ok	ok	ok	ok
12/18/96	12:14:57	Reform	353H6	yes		ok	ok	ok	ok
12/18/96	12:58:38	Reform	353H7	yes		ok	ok	ok	ok
12/19/96	7:47:52	Reform	354CS	yes		ok	ok	ok	ok
12/19/96	7:47:52	Reform	354H1	yes		ok	ok	ok	ok
12/19/96	9:18:51	Reform	354H2	yes		ok	ok	ok	ok
12/19/96	10:15:28	Reform	354H3	yes		ok	ok	ok	ok
12/19/96	10:59:24	Reform	354H4	yes		ok	ok	ok	ok
12/19/96	11:45:20	Reform	354H5	yes		ok	ok	ok	ok
12/19/96	12:34:16	Reform	354H6	yes		ok	ok	ok	ok
12/19/96	13:18:06	Reform	354H7	yes		ok	ok	ok	ok
12/20/96	7:34:07	Reform	355CS	yes		ok	ok	ok	ok
12/20/96	7:34:07	Reform	355H1	yes		ok	ok	ok	ok
12/20/96	9:13:03	Reform	355H2	yes		ok	ok	ok	ok
12/20/96	10:01:01	Reform	355H3	yes		ok	ok	ok	ok
12/20/96	10:49:23	Reform	355H4	yes		ok	ok	ok	ok
12/20/96	11:35:51	Reform	355H5	yes		ok	ok	ok	ok
12/20/96	12:27:08	Reform	355H6	yes		ok	ok	ok	ok
12/20/96	13:09:36	Reform	355H7	yes		ok	ok	ok	ok
1/7/97		Pre-93	7header						
1/8/97	8:12:48	Pre-93	8CS	yes	yes	ok	ok	ok	ok
1/8/97	8:12:48	Pre-93	8H1	yes	yes	ok	ok	ok	ok
1/8/97	9:53:41	Pre-93	8H2	yes	yes	ok	ok	ok	ok
1/8/96	10:40:19	Pre-93	8H3	yes	yes	ok	ok	ok	ok

1/8/97	11:22:11	Pre-93	8H4	yes	yes	ok	ok	ok	ok
1/8/97	12:09:51	Pre-93	8H5	yes	yes	ok	ok	ok	ok
1/8/97	13:01:52	Pre-93	8H6	yes	yes	ok	ok	ok	ok
1/8/97	13:42:20	Pre-93	8H7	yes	yes	b	ok	ok	ok
1/9/97	7:52:22	Pre-93	9CS	yes	yes	ok	ok	ok	ok
1/9/97	7:52:22	Pre-93	9H1	yes	yes	ok	ok	ok	ok
1/9/97	9:44:30	Pre-93	9H2	yes	yes	ok	ok	ok	ok
1/9/97	10:28:00	Pre-93	9H3	yes	yes	ok	ok	ok	ok
1/9/97	11:09:16	Pre-93	9H4	yes	yes	ok	ok	ok	ok
1/9/97	11:56:33	Pre-93	9H5	yes	yes	ok	ok	ok	ok
1/9/97	12:44:18	Pre-93	9H6	yes	yes	ok	ok	ok	ok
1/9/97	13:29:57	Pre-93	9H7	yes	yes	ok	ok	ok	ok

a - Cover page of test report printout is missing; data recovered from emission summary pages of test report.

b - Hardcopy printout is missing from archive; no data quality problems were noted by emissions test operator; data for these tests are consistent with data for the other tests of this fuel .

NO_x - Span checks for NO_x analyzer were slightly above tolerance, ranging from 2% to 5% of full scale. Other QC results are within tolerance. Emission results for these tests are consistent with the emission rates from the other 44 emission tests on this fuel.

Audits

The following external audits were conducted as part of this program:

1. Instrument train verification conducted by CARB El Monte laboratories on 5/16/96 with the following results (ARB, 1996):
   -NOx linearity test – pass
   -NOx conversion efficiency test found to be 98.96%-pass
   -Analyzer accuracy using NIST gases

Instrument/Range	% Difference	Status
NOx 100ppm	-0.21	Pass
NOx 300ppm -	0.93	Pass
NOx 1000ppm	+1.58	Pass
CO_2 1%	+1.06	Pass
CO_2 6%	-0.03	Pass
CO 100ppm	+3.30	Fail
CO 300ppm -	0.87	Pass
CO 1500ppm	+5.22	Fail

   -THC analyzer was not verified because the instrument ran out of zero pot.
   -Barometric readings were verified with +0.06% difference-Pass

   Corrective Action: A follow-up Verification/Inspection was conducted by ARB on May 20, 1996. All instruments passed. CVS propane injection/recovery passed.

2. Instrument train verification conducted by CARB El Monte laboratories on 1/16/97 with the following results (ARB, 1997):
   -Analyzer accuracy using NIST gases

Instrument/Range	% Difference	Status
HC 100ppm	-1.229	Pass
	-0.198	Pass
CO 100ppm	+0.770	Pass
	+0.862	Pass
CO 300ppm	-0.019	Pass
	+0.131	Pass
CO_2 1%	+3.409	Fail
CO_2 6%	-8.9574	Fail
NOx 100ppm	-1.686	Pass
NOx 300ppm	+0.477	Pass
	+0.543	Pass

   Corrective Action: LACMTA was actioned to correct the problem with the CO_2 analyzer. LACMTA found that a span cylinder had been changed, but the span point had not been updated. This was done and a new calibration conducted. A follow-up visit was conducted by CARB on 1/23/97 with the following results:

CO_2 1%	+0.633	Pass
	+0.626	Pass
CO_2 6%	-0.155	Pass
	+0.316	Pass

Corrective Action: It was determined from LACMTA that the problems with the CO_2 span had occurred on January 6, 1997 and affected the CO_2 emission results obtained on January 8 and 9, 1997. The CO_2 emission results for these dates were corrected with the new calibration numbers.

Estimation of Accuracy, Precision, and Detection Limit

The accuracies shown in Table 1-3 are based upon meeting the audit tolerance of 2%. The precisions are based upon replicate test variability. The detection limits are calculated as two times the standard deviation of zero checks for a random sample of twenty zero checks. The values were converted to g/bhp-hr using nominal values for total CVS flow and total power.

3.4 Sample collection

Calibrations

The flow meters used for PTFE (elemental analyses) and Quartz Fiber (ion and carbon analyses) were calibrated with a dry gas meter traceable to NIST prior to sampling.

The Method 5 box used for particle size samples contains a dry gas meter. This meter was cross checked against a NIST traceable dry gas meter.

Audits

Dick Munns Company conducted an audit of the CVS system and the flow controllers on the secondary dilution tunnel on April 22, 1997 with the following results (Dick Munns Co., 1997):

-CVS flow found to be within 2% of calibration value-Pass
-Mass flow controllers on secondary dilution tunnel found to be within 2% of calibration values-Pass

Tunnel Backgrounds

Three dilution tunnel background samples were collected during testing. The following emission rates were obtained with the tunnel blanks:

1. 1.78 mg/bhp-hr equivalent
2. 1.90 mg/bhp-hr equivalent
3. 1.78 mg/bhp-hr equivalent

All tunnel backgrounds were <1% of the engine emission rates

3.5 Particle analyses

Cahn Microbalance

The microbalance was used for determination of particle size distributions. Results of periodic balance checks are as follows:

	Zero Check	Calibration Check (200mg)	Reference Filter Checks			
			Ref #1	Ref #2	Ref. #3	Ref. #4
Av. (mg)	-0.001	199.995	76.219	75.97	136.67	135.681
S. D. (mg)	0.002	0.003	0.002	0.004	0.003	0.005

Blanks

Three PTFE filter/trip blanks were supplied to DRI. These were used as matrix blanks. I.e., X-ray spectral backgrounds were subtracted using average spectra from the three filter/trip blanks.

One quartz filter/trip blank was supplied to DRI. This was used as a matrix blank,i.e., concentrations for ion and carbon analyzes were blank subtracted using the filter/trip blank.

Tunnel Backgrounds

Two PTFE and three quartz fiber tunnel background samples were collected and analyzed. The results of these analyses after matrix blank subtraction are summarized below and compared with the lower detection limits in units of mg/bhp-hr.

	Detection Limit	*Average Tunnel Background*
	mg/bhp-hr	*mg/bhp--hr*
Chloride	0.124	0.083
Nitrate	0.124	0.029
Sulfate	0.124	0.015
Ammonium	0.124	0.000
Organic Carbon	0.248	1.769
Elemental Carbon	0.248	0.189
Na	0.025	0.079
Mg	0.025	0.027
Al	0.025	0.017
Si	0.015	0.017
P	0.015	0.014
S	0.010	0.003
Cl	0.025	0.003
K	0.015	0.002

Ca	0.010	0.006
Ti	0.010	0.000
V	0.005	0.000
Cr	0.005	0.000
Mn	0.004	0.000
Fe	0.004	0.002
Co	0.002	0.000
Ni	0.002	0.000
Cu	0.003	0.000
Zn	0.005	0.001
Ga	0.005	0.000
As	0.005	0.000
Se	0.003	0.000
Br	0.003	0.000
Rb	0.003	0.000
Sr	0.003	0.000
Y	0.003	0.000
Zr	0.005	0.000
Mo	0.005	0.000
Pd	0.025	0.000
Ag	0.030	0.000
Cd	0.030	0.005
In	0.030	0.006
Sn	0.040	0.010
Sb	0.045	0.013
Ba	0.125	0.033
La	0.130	0.006
Au	0.015	0.000
Hg	0.005	0.001
Tl	0.005	0.000
Pb	0.005	0.000
Ur	0.005	0.000

Only organic carbon, Na, and Mg were found in the tunnel background samples at levels higher than the detection limits. The sum of all species identified in the tunnel background samples is less than 1.5% of that found in the engine exhaust samples. Engine analysis results were corrected for tunnel backgrounds.

Estimation of Accuracy , Precision, and Detection Limit

The accuracies shown in Table 1-3 for Total PM are based upon meeting the audit flow rate tolerances of 2%. Balance errors were assumed to be negligible. Total PM requires two flow rates (sample flow and CVS flow), thus accuracy is given as 2%*sqrt(2). Particle size fractions are relative measurements and do not depend on flow rates; on the basis of balance data alone,

accuracy is better than 1% of total mass. Accuracy data for elements, ions, and EC/OC have not been determined.

The precisions for all particle species measurements are based upon replicate test variability.

The detection limits for Total PM and for particle size fractions are results for tunnel blanks. For particle size fractions these are conservative compared to the detection limit determined from microbalance QC data. The detection limits for elements, ions, and EC/OC are calculated as two times the average analytical uncertainties reported by DRI. These are consistent with the analytical results from analysis of tunnel blank samples.

3.6 Speciated hydrocarbons

Hydrocarbons were analyzed by gas chromatography: one for C1-C4 and one for C4-C12 species. The systems were calibrated using propane in a 23-component mixture and the response was checked against the component in the mixture. Response factors for a selection of species was routinely monitored during the course of the study. Table 3-1 shows the mean response, standard deviation, bias, and coefficient of variation for those species. Propane is included twice because it was measured on both the light end and heavy end GC. Precision and accuracy were within tolerance throughout the range.

Table 3-1 Speciated HC Analytical Precision

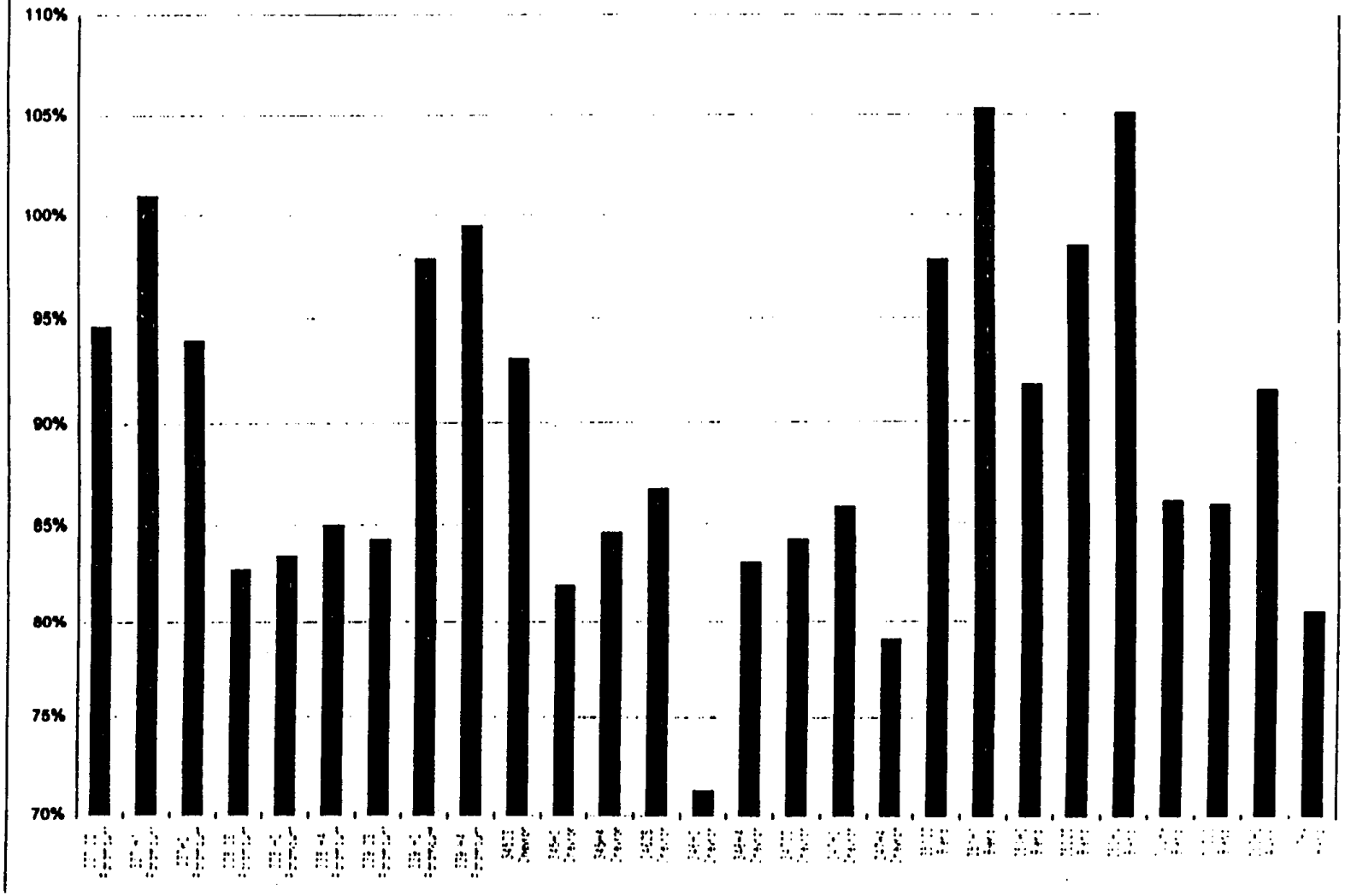
Species	True ppm	Mean Response ppm	Std. Dev ppm	Bias %	CV %
methane	5.16	5.16	0.01	-0.1%	0.1%
ethane	5.05	5.19	0.06	2.8%	1.1%
propane	9.18	9.18	0.00	0.0%	0.0%
13-butadiene	4.70	4.54	0.10	-3.4%	2.1%
propane	9.18	9.18	0.01	0.0%	0.1%
butane	5.08	4.98	0.10	-2.0%	1.9%
benzene	4.93	5.05	0.12	2.4%	2.4%
224tmp	4.98	4.92	0.07	-1.2%	1.4%
toluene	5.00	4.93	0.09	-1.5%	1.9%
decane	5.38	5.08	0.19	-5.6%	3.5%

The method employed for speciated hydrocarbon sampling specifies a tolerance of 80% recovery for the sum of hydrocarbon species as compared with the total hydrocarbons measured by FID analysis of the integrated emissions bag sample. Results for this study are shown in Figure 3-1. Two samples had recoveries of about 79% and 71 %. The sample with 71% had a GC-derived methane value that was suspiciously low. It was less than half the methane value observed for other samples in the same category. All other recoveries were >80%.

Estimation of Accuracy, Precision, and Detection Limit

The accuracies shown in Table 1-3 for speciated HC are based upon the mean bias observed for the response to the 23-component standard. The precisions are calculated as the standard deviation of the responses to the 23 component species. Detection limits are based upon the minimum peak area (minimum concentration) registered by the GC peak integration software, which is less than 0.01 ppmC.

Figure 3-1. MTA FID and CE-CERT GC Recovery



3.7 Carbonyls

Carbonyls were collected at 1 LPM onto Sep-pak cartridges, extracted into acetonitrile, and analyzed by HPLC. Precisions are estimated from calibration standard data. These precisions are estimated from data at a concentration of 3.0 µg/ml (about 60 mg/bhp-hr). This is appropriate for formaldehyde, but provides conservative upper limits for the remaining species in this study.

An analytical blank and a two-point calibration (3.0 µg/ml and 30.0 µg/ml) were performed at the beginning of each analytical run, and a calibration curve generated for each species. Analytical blanks were below detection limits (i.e., no HPLC peak) in all cases. To estimate bias and precision, peak areas for the 3.0 µg/ml calibration standard were then converted to µg/ml based on the calibration equation obtained. The mean and standard deviations of these data are shown in Table 3-2. Bias is calculated as mean minus 3.0 and CV, coefficient of variation, is the standard deviation divided by the mean.

Table 3-2 Carbonyl Analytical Precision

Calibration Precision					
x	Mean	Std. Dev.	Bias	CV	$CV_{Mulliday}$
x	µg/ml	µg/ml	%	%	%
formaldehyde	2.97	0.037	-0.9%	1.2%	1.1%
acetaldehyde	2.97	0.023	-0.9%	0.8%	1.3%
acrolein	3.00	0.039	0.1%	1.3%	1.9%
acetone	3.03	0.084	1.0%	2.8%	2.8%
propionaldehyde	2.93	0.035	-2.2%	1.2%	2.4%
crotonaldehyde	2.97	0.113	-0.9%	3.8%	4.7%
methacrolein	3.02	0.090	0.7%	3.0%	2.0%
MEK	3.05	0.149	1.6%	4.9%	4.6%
butyraldehyde	2.87	0.173	-4.5%	6.0%	4.9%
benzaldehyde	2.92	0.020	-2.8%	0.7%	1.4%
valeraldehyde	2.83	0.078	-5.6%	2.7%	3.7%
tolualdehyde	2.96	0.031	-1.4%	1.0%	1.4%
hexaldehyde	2.82	0.145	-6.0%	5.1%	6.2%

Calibration performance during the course of an analytical run was also checked in a second way, based on the stability of the HPLC response factors from day to day. Based on the response factors for each of the six analytical run days, an average response factor was calculated. Response to injection of the calibration standards for each of these six days were then calculated using the overall average response factor. These data represent the variability in response that would occur if the analyzer were not recalibrated each day. In this way the calibration standards injected each day can be considered QC controls having a variability that will place an upper limit on the variability within a given day. These results are labeled $CV_{Mulitday}$ in Table 3-2. They demonstrate that the precision calculated from the initial calibration is reasonable, and that it is representative of the entire analytical run.

The analytical precisions were converted to emission units (mg/bhp-hr) and compared with typical concentrations in Table 3-3. Carbonyl emissions are calculated as the difference between a tunnel sample and a background sample. Thus, in Table 1-6, the precisions shown in Table 3-2 were multiplied by the square root of 2, to represent the precision of the net difference. For formaldehyde and acetaldehyde, the precisions are comparable with the variability of replicate testing. For the species measured at low concentrations, the precisions tend to be overestimates for two reasons. First, the precisions were estimated at 3.0 µg/ml; lower concentrations would yield smaller precisions. Second, the net carbonyl is a difference between sample and background samples; precisions for both samples were taken into account, but in fact the background samples were generally near zero and do not contribute to imprecision. The replicate test data show smaller precisions, and thus support the assertion that the relative precision estimates derived above are too large.

Table 3-3. Carbonyl Emission Rate Precisions

Background Corrected Sample Precision			
	Typical Emissions	Std. Dev. for Background Corrected Data	
	mg/bhp-hr	mg/bhp-hr	% of typical
formaldehyde	58.72	1.01	1.7%
acetaldehyde	19.17	0.64	3.3%
acrolein	3.43	1.07	31.2%
acetone	6.43	2.30	35.8%
propionaldehyde	4.04	0.96	23.7%
crotonaldehyde	1.71	3.07	179.4%
methacrolein	0.09	2.45	-

MEK	0.00	4.06	-
butyraldehyde	4.08	4.73	116.0%
benzaldehyde	1.74	0.54	30.9%
valeraldehyde	0.82	2.13	-
tolualdehyde	3.38	0.84	24.7%
hexaldehyde	0.47	3.95	-

Estimation of Accuracy , Precision, and Detection Limit

The accuracies shown and precisions shown in Table 1-3 for speciated carbonyls are for the four toxic species of interest: formaldehyde, acetaldehyde, acrolein, and propionaldehyde. The accuracy is based upon the mean bias observed for the response to the 13-component standard. The precisions are calculated as the standard deviation of the responses to the 13-component species. Detection limits are based upon the minimum peak area (minimum concentration) registered by the HPLC peak integration software, which is less than 0.02 µg/ml.

3.8 Particulate-bound PAH and Nitro-PAH

Introduction

A sampling system consisting of a high volume filter backed by PUF plugs was used to collect samples for PAH and nitro-PAH analysis by GC-MS at SAPRC. Lists of toxic particle-bound and gas-phase PAH and nitro-PAH to be targeted for analysis were developed by the California Air Resources Board. Of the 20 PAH targeted for analysis in the particulate matter, 19 have been quantified. Only picene was not quantified, due to the lack of an available standard. Of the 19 semi-volatile PAH targeted for analysis, 15 were quantified in the filter and PUF plug samples. The four remaining semi-volatile PAH, acenaphthene, acenaphthylene and 1- and 2-methylnaphthalene, were not collected quantitatively on the high volume filter backed by PUF plugs sampling system. These last PAH were, however, quantitatively collected by the UCD XAD-backed sampling system.

Six nitro-PAH were targeted for analysis in the particulate matter and two (1-nitropyrene and 6-nitrobenzo[a]pyrene) were detected and quantified. Upper limits (nitro-PAH < specified value) were provided for the remaining four particle-associated nitro-PAH on the target list. Seven semi-volatile nitro-PAH and the methynitronaphthalenes were targeted for analysis. 9-

Nitroanthracene (although listed as a semi-volatile nitro-PAH) was detected and quantified in the filter samples and 1- and 2-nitronaphthalene were detected and quantified in the PUF samples. Upper limits for the remaining semi-volatile nitro-PAH based on the estimated detectable levels were provided.

The collection and storage of samples followed specifically defined procedures. All testing conditions were recorded on Field Data Sheets while sampling at the LACMTA facility. For each sampling run, the date, time, flow rate, temperature and pressure of the sampling system was recorded. All samples were identified in a Master Log.
Transfer of the intercomparison samples and HPLC fractions for mutagenicity analysis between SAPRC and UCD were tracked with Chain of Custody forms. Samples were shipped by overnight carrier and were cooled by blue ice during shipment.

Blanks and Spike Recovery

A cleaned filter and a trip blank filter were spiked with the deuterated IS in similar µg levels to the emission sample filters. No non-deuterated PAH were detected in these samples, verifying both the trip blank and the absence of any interferences from the deuterated standards.
A cleaned filter was also spiked with the deuterated internal standards and SRM 1491 to verify the quantification of the PAH targeted present in NIST SRM 1491 (aromatic hydrocarbons in hexane/toluene). The filter was treated as if it were a sample and was Soxhlet extracted, concentrated and analyzed by GC-MS with SIM. The internal standards and quantitation ions were as listed in Table 10 of the main report. Table 3-4 lists the measured PAH on the filter and the % difference values from the amounts spiked.

Frequent GC-MS blank runs in which only solvent was injected were run. These blanks occurred between fuel types and before and after standard solutions were run. In no case was detectable carry over between runs observed.

Calibration Standards

Analysis of the screening samples (see Table 5 of the main report) allowed the deuterated PAH spikes to be added to the filter and PUF samples at levels comparable to those of the analytes. Calibration standards were designed to bracket the amounts present in the samples. For PAH quantification, calibration curve and response factor standards of 5-10 ng/µl were prepared from NIST SRM 1491 (aromatic hydrocarbons in hexane/toluene) and a master stock solution of

deuterated PAH and nitro-PAH in methylene chloride. Concentration ratios of 0.5:1, 1:1, and 2:1 were used for the calibration curve solutions. Milligram amounts of deuterated PAH and nitro-PAH standards were weighed on a small pan in a Cahn Model 25 Electrobalance and master stock solutions were prepared in 50 and 100 ml volumetric flasks. The solutions were wrapped with aluminum foil, sealed with teflon tape and stored in a freezer at -20 C. Calibration curve solutions were prepared from the SRM and the stock solutions using a Hamilton Gastight syringe. The solutions were stored in 2 ml amber vials with teflon-backed septa. Aliquots were transferred as needed into 2 ml autosampler vials for use in the Hewlett-Packard 7673A Autosampler. Standard solutions were prepared periodically as needed and to ensure the integrity of the solution concentration.

Deuterated compounds used as standards are: naphthalene-d_8, acenaphthene-d_{10}, anthracene-d_{10}, benzo[a]pyrene-d_{12}, chrysene-d_{12}, dibenz[a,h]anthracene-d_{14}, fluoranthene-d_{10}, perylene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, 1-nitronaphthalene-d_7, 1-nitropyrene-d_9, and 2-nitrofluorene-d_9.

Table 3-4. PAH Recovery from Spiked Filter.

Polycyclic Aromatic Hydrocarbon	Spike (µg)	Recovered (µg)	% Difference[a]
phenanthrene	7.01	6.69	-4.6
anthracene	7.82	7.89	0.8
1-methylphenanthrene	7.00	6.99	-0.2
fluoranthene	5.91	5.90	-0.3
pyrene	5.89	6.11	3.7
benz[a]anthracene	3.59	2.69	-25.2
chrysene	7.03	7.61	8.3
benzo[b]fluoranthene	5.25	5.62	7.0
benzo[k]fluoranthene	5.57	7.45	33.8
benzo[e]pyrene	5.62	7.20	28.1
benzo[a]pyrene	6.79	7.91	16.4
perylene	7.12	8.03	12.8
indeno[1,2,3-cd]pyrene	6.29	6.09	-3.3
dibenz[a,h]anthracene	5.18	5.68	9.7
benzo[ghi]perylene	5.29	5.71	7.8

[a]Calculated as [(Recovered - Spiked)/Spiked] x 100.

Three PAH response factor standards were prepared in 50 ml volumetric flasks for the quantification of higher molecular weight PAH. Solutions were made using a Cahn Electrobalance, sealed and stored using the same procedure as the above volumetric solutions. Each solution in methylene chloride contained 5-10 ng/µl of chrysene-d_{12}, benzo[a]pyrene-d_{12}, and dibenz[a,h]anthracene-d_{14} plus the following PAH: solution #1, cyclopenta[cd]pyrene, benzo[c]phenanthrene, indeno[1,2,3-cd]pyrene, coronene, dibenzo[a,e]pyrene, and benzo[b]chrysene; solution #2, benzo[c]chrysene, dibenzo[a,h]pyrene; solution #3, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, dibenz[a,c]anthracene, and dibenz[a,j]anthracene.

The deuterated nitro-PAH spikes were added at levels expected based upon the amount of PAH present in the screening samples and the relative amount of nitro-PAH/PAH present in the NBS SRM 1650, Diesel Particulate. The actual nitro-PAH present in the samples were at levels lower than the expected values based on the SRM. Therefore, for quantification of nitro-PAH, two stock solutions were prepared of SRM 1587 (nitro-PAH in methanol) and 7.8 ng/µl 1-nitropyrene-d_9. One solution contained a 10-fold dilution of SRM 1587 (approximately 0.7 ng/µl) and the other solution a 50-fold dilution of the SRM (approximately 0.14 ng/µl). Solutions were stored in 2 ml amber vials as above. In addition a calibration solution containing approximately 3 ng/µl each 1-nitronaphthalene-d_7 and 2-nitrofluorene-d_9, 0.15 ng/µl each 1-nitronaphthalene and 2-nitronaphthalene plus a 100-fold dilution of SRM 1587 (~0.07 ng/µl) was prepared for quantification of nitro-PAH on the PUFs.

Instrument Control and Maintenance

Prior to running each group of samples and standards, the instrument was Autotuned and if the tune parameters were not satisfactory, the instrument source was cleaned.

If the GC peak shapes broadened and/or the column resolution decreased for the standard or sample peaks, inlet maintenance was performed, generally including changing the pre-column and the silylated glass-wool in the split/splitless injector.

Calibration standards were run prior to beginning the sample injections and periodically throughout the sample analysis. Any changes in the measured response factors [(area/ng PAH)/(area/ng deuterated PAH)] were generally associated with changes in the peak shapes and were corrected by inlet and pre-column maintenance.

Occasionally, the HP 7673A Automatic Sampler would not inject properly (perhaps an air bubble in the syringe, etc.) and less than the specified amount was injected. If no peaks were detected, the sample was re-run. However, in a few instances the more abundant analytes were detected and the sample was not repeated. In no case were fewer than replicate injections and peak areas used. Triplicate area counts were obtained and averaged for >99% of the analyte quantifications.

Fifty percent of each filter and front PUF and 37.5% of each back PUF extract was fractionated by HPLC and the appropriate fraction was analyzed by GC-MS for nitro-PAH. Again, all GC-MS injections were made in triplicate. For nitro-PAH analysis, on-column injection was necessary to achieve good compound response. Previously it was found that the autosampler run in the on-column mode would often result in carry-over between injections. All nitro-PAH analysis were, therefore, performed by manual cool, on-column injection using a syringe fitted with an approximately 6 in. fused silica needle that allowed the sample to be directly deposited into the deactivated fused-silica pre-column. Triplicate area counts were obtained and averaged for 100% of the nitro-PAH quantifications.

Replicates

For each of the three fuel types three independent replicate samples, as noted in Table 1, were collected and analyzed. Each replicate sample consisted of a filter, a front PUF and a back PUF to be analyzed. Analysis of PAH by GC-MS was conducted utilizing a 25% aliquot of each of the 9 filter, 9 front PUF and 9 back PUF extracts. All GC-MS injections were made in triplicate. For the filter samples, two series of GC-MS analyses were conducted to quantify the full molecular weight range of targeted PAH. The calibration standards used for these quantifications are detailed above.

Analysis of nitro-PAH by GC-MS was conducted on HPLC fraction #4 in which the nitro-PAH have been shown to elute. The nine filter HPLC fraction #4's and 9 front PUF HPLC fraction #4's were analyzed by triplicate GC-MS injections. The 9 back PUF HPLC fraction #4's were only injected once each, because no nitro-PAH were detected.

Table 3-5 lists the results of the PAH analyses for the three replicate two-cycle filter with PUF samples collected for each of the three fuel types. Table 3-6 lists the results of the nitro-PAH analyses. Tables 30 and 31 in the main report give the average emission rate and standard

deviations based on the three replicate 2-cycle sample collections for each fuel type. Figures 14-20 in the main report show the means and 95% confidence intervals for each of the analytes.

Summary of Departures

No standardized test methods were available for the analysis of PAH and nitro-PAH in diesel samples. Methods previously successfully applied to ambient samples analyses (Final Report to CARB Contract No. A5-185-32; Atkinson *et al.*, 1988) were used. The procedures are summarized in the body of this report and no departures from these protocols were noted.

SAPRC/UC Davis PAH Intercomparison

In the October 1996 Pretest, three samples were taken: a single-cycle sample and two two-cycle samples. One of the two-cycle samples was allocated for a SAPRC-UCD intercomparison analysis. The other two samples were allocated to an exploratory analysis to determine how much sample would be required for the main study.

The two filters (front and back) for the intercomparison sample were cut in half and SAPRC retained half of each filter and the remaining halves were shipped to UCD. First, the total weight of the particulate matter was determined by weighing. Immediately before cutting each filter was weighed and after cutting the two halves were weighed to determine the amount of particulate matter represented by each half.

The results of this intercomparison are given in Table 3-7 and show good agreement between the two laboratories for the PAH quantified. Further intercomparisons of results where individual semi-volatile PAH were measured independently by the two laboratories are discussed in the body of the report.

Table 3-5. Emission Rates for Polycyclic Aromatic Hydrocarbons.

PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3 µg/bhp-hr	338H4,H5 µg/bhp-hr	338H6,H7 µg/bhp-hr	346H5,H6 µg/bhp-hr	347H3,H4 µg/bhp-hr	347H5,H6 µg/bhp-hr	351H3,H4 µg/bhp-hr	352H3,H4 µg/bhp-hr	353H5,H6 µg/bhp-hr
2,3,5-trimethylnaphthalene[a,b]	289.12	278.60	283.31	15.49	12.07	16.74	58.94	56.40	53.31
phenanthrene[c]	332.81	347.09	330.23	152.05	178.86	151.84	173.66	210.89	277.64
anthracene[d]	37.26	39.50	39.92	16.73	20.89	18.01	20.33	24.43	33.72
Me-phenanthrenes/anthracenes[c,e]	313.02	343.10	337.86	26.76	24.70	24.05	90.01	101.44	144.50
fluoranthene[d]	137.03	122.55	125.77	124.29	153.31	119.49	95.31	126.50	147.40
pyrene[d]	210.44	177.60	191.05	195.57	253.81	184.18	163.44	217.87	239.15
benzo[c]phenanthrene	3.26	3.05	2.78	1.65	1.89	1.67	1.31	1.49	1.82
benzo[ghi]fluoranthene[f]	27.93	23.40	23.20	17.14	21.30	18.35	14.61	16.98	19.22
cyclopenta[cd]pyrene	25.71	17.51	21.11	24.04	29.74	24.67	17.99	20.87	24.89
benz[a]anthracene	16.19	14.87	18.19	10.74	11.62	9.34	8.17	12.51	12.19
chrysene + triphenylene[g]	17.14	15.82	19.11	9.94	10.98	10.21	9.08	14.11	13.41
benzo[b+j+k]fluoranthene[g]	30.93	26.95	35.28	21.09	23.37	25.04	20.94	36.76	29.85
benzo[e]pyrene	17.07	13.83	19.22	13.57	16.08	14.00	13.54	24.69	18.73
benzo[a]pyrene	21.39	16.82	23.15	14.90	18.02	16.53	14.59	26.05	21.14
perylene	4.55	3.35	5.05	2.92	4.38	3.82	2.95	5.25	4.36
indeno[1,2,3-cd]fluoranthene	0.41	0.33	0.28	0.24	0.19	0.22	0.17	0.17	0.17
benzo[c]chrysene	0.28	0.24	0.34	0.21	0.13	0.22	0.11	0.13	0.19
dibenz[a,j]anthracene	0.89	0.99	0.92	0.65	0.45	0.56	0.57	0.69	0.75
indeno[1,2,3-cd]pyrene	19.99	16.51	21.84	16.23	12.33	13.57	14.26	32.12	20.10
dibenz[a,h + a,c]anthracene[g]	1.53	1.40	1.70	0.94	0.73	0.93	0.90	2.22	1.34
benzo[b]chrysene	0.39	0.41	0.39	0.21	0.13	0.12	0.22	0.28	0.32
benzo[ghi]perylene	50.47	38.97	58.09	48.15	35.51	35.77	39.09	90.44	52.70
coronene	13.04	8.33	7.10	5.04	4.42	5.33	5.98	9.14	7.32
dibenzo[a,l]pyrene	3.28	2.84	2.39	1.42	1.24	1.11	1.81	2.35	2.77
dibenzo[a,e]pyrene	1.40	1.08	0.83	0.68	0.60	0.56	0.96	1.25	1.19
dibenzo[a,i]pyrene	1.14	0.85	0.73	0.18	0.34	0.31	0.55	0.76	0.83
dibenzo[a,h]pyrene	1.62	1.22	1.15	0.83	0.75	0.68	0.61	0.91	1.00

Table 3-7. Emission Rates for Polycyclic Aromatic Hydrocarbons (cont.).

[a] Lower limit based on summing amounts on front PUF and back PUF (amount on filter negligible).
[b] The area of the molecular ion peak (m/z 170) and the response factor for 2,3,5-trimethylnaphthalene relative to deuterated phenanthrene were used to quantify 2,3,5-trimethylnaphthalene and a co-eluting isomer.

[c] Sum of amounts on filter, front PUF and back PUF.
[d] Sum of amounts on filter and front PUF; negligible amount found on back PUF.
[e] The areas of the molecular ion of the five isomers present were summed and the response factor for 1-methylphenanthrene relative to deuterated phenanthrene was used to quantify all isomers.
[f] Standard not available, response factor for cyclopenta[cd]pyrene relative to deuterated chrysene used for quantification.
[g] Co-eluting isomers.

Table 3.6. Emission Rates for Nitro-Polycyclic Aromatic Hydrocarbons.

Nitro-PAH	PRE-1993 FUEL			LOW AROMATIC FUEL			REFORMULATED FUEL		
	338H2,H3 µg/bhp-hr	338H4,H5 µg/bhp-hr	338H6,H7 µg/bhp-hr	346H5,H6 µg/bhp-hr	347H3,H4 µg/bhp-hr	347H5,H6 µg/bhp-hr	351H3,H4 µg/bhp-hr	352H3,H4 µg/bhp-hr	353H5,H6 µg/bhp-hr
1-nitronaphthalene	0.53	0.53	0.50	0.34	0.31	0.31	0.44	0.48	1.07
2-nitronaphthalene	1.50	1.53	1.51	0.64	0.68	0.74	1.13	1.17	1.80
methylnitronaphthalenes	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
4-nitrobiphenyl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
5-nitroacenaphthene	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
2-nitrofluorene	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
9-nitroanthracene[a]	0.56	0.62	0.50	0.56	0.54	0.53	0.30	0.28	0.44
1-nitropyrene	2.10	2.13	1.64	2.00	2.20	2.01	1.23	2.08	1.61
3-nitrofluoranthene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
4-nitropyrene	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
7-nitrobenz[a]anthracene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrochrysene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6-nitrobenzo[a]pyrene	0.32	0.39	0.22	0.47	0.41	0.39	0.31	0.45	0.43

[a]For the Pre-1993 Fuel and the Reformulated Blend, interferences prevented quantification using the molecular ion at m/z 223 and the $[M-NO]^+$ fragment ion was used.

Table 3-7. PAH Measured on Intercomparison Filter.

Polycylic Aromatic Hydrocarbon	SAPRC ng/mg	UCD ng/mg	% Difference[a]
phenanthrene	90	110	19
anthracene	18	26	35
Me-phenanthrenes/anthracenes	133	169	24
fluoranthene	231	262	13
pyrene	448	556	21
benz[a]anthracene	97	-	-
chrysene + triphenylene	75	-	-
sum of 228 dalton species[b]	172	189	9
benzo[b+j+k]fluoranthene	160	179	11

[a]Calculated as [(UCD value - SAPRC value)/ Average value] x 100.

[b]At SAPRC separate values determined for 228 Dalton species benz[a]anthracene and chrysene + triphenylene.

3.9 NITROSAMINE QUALITY ASSURANCE

Introduction

A screening test for nitrosamine was conducted at the MTA facility. Nitrosamine analysis was performed by Lancaster Laboratories. A summary of the QA procedures are given below.

Blanks

Trip blank. One trip blank was collected. A capped Thermosorb-N cartridge was taken to the MTA facility. The cartridge remained at the facility until Nitrosamine sampling was completed. The trip blank was sent along with the samples to Lancaster laboratories for analysis. Listed in Table 3-8 are tunnel and trip blank results.

Table 3-8. Tunnel and Trip Blanks Results

Nitrosamine	Trip Blank (ng/cart)	Tunnel Blank (ng/cart)
NDMA	<20	<20
NDEA	<20	<20
NDPA	<20	<20
NDBA	<30	<30
NPIP	<20	<20
NPYR	<20	<20
NMOR	<20	<20

Calibration Standards

All nitrosamine certified standards were obtained from Chem Services.

Laboratory control spikes

Laboratory control spikes LC1 and LC2 were run with each batch of samples. Two Thremosorb-N samples were each spiked with 50 ppb of nitrosamines. The relative percent difference between the two samples must be within 20%. Analysis of samples could be done when laboratory check samples were within 20%. If the difference is outside the control range

the problem must be corrected before the samples are run. All samples that were reported were within the 20% cutoff criteria.

Replicates

Duplicate exhaust samples from the reformulated fuel and pre-1993 fuel were taken. Results are presented in Table 3 of the Results section in the main body of the report. Duplicate values in the study were near or at the detection limit and were below CARB's Monitoring Laboratory Division Quality Assurance section recommended levels for comparision. Standard laboratory practices as recommended by CARB requires the comparision of duplicate when values are greater or equal to five times the LOD.

Limit of Detection (LOD) and Calibration Curve.

The limit of detection was defined as 3:1 signal to noise.

The five point calibration curve ranged from 25 ppb to 500 ppb.

To ensure the instrument was in control the following procedure was run prior to the analysis of each batch of samples.

A 5 point calibration curve must be run prior to analysis of a batch of samples.

laboratory control spikes LC1 and LC2 must be within 20% prior to the analysis of samples.

Instrument Maintenance and Modification Summary

The laboratory did not report any major maintence or modification during the study.

Summary of Departures from Current Method and SOP

OSHA method 27 was used to analyze nitrosamines. One departure from the method was to replace the column specified in the method with a Restek Stablewax .53 ID 30 meter column to improve chromatography.

3.10 VAPOR PHASE PAH QUALITY ASSURANCE

Introduction

A test for vapor-phase PAHs was conducted at the MTA facility. Vapor phase PAH sampling and analysis was performed by UCD. Both high volume and low volume samplers were used to collect PAHs. Analysis of samples was performed by UCD. A summary of the QA procedures are given below.

Trip Blanks.

Two trip blank trains were collected, one for the high volume sampler and one for the low volume sampler. The train consisted of two filters and a sorbant containing both PUF and XAD. Prior to sampling the high volume sorbant cartridges and filters were wrapped in aluminum foil. Prior to sampling the low volume sorbant cartridges were sealed in Teflon containers with screw caps and the filters were placed between glassine paper and stored in a box. The filters and sorbant modules were taken to the MTA facility. The cartridge remained at the facility until PAH sampling was completed. The trip blank along with the samples were shipped and stored at ^{0}C at UCD until analysis.

Tunnel Blanks.

Three low volume and three high volume tunnel blanks were collected from the tunnel while the CVS fan on the tunnel was turned on and the engine turned off. One low volume and one high volume tunnel blank was taken prior to the start of the exhaust sampling with the diesel engine running on a new fuel. Given in Tables 3-9 and 3-10is the analysis of the tunnel and trip blanks.

Table 3-9. Blank levels in XAD Samples

Sample ID	Tr157	UL100	UL120	UL134	TR1PV	UL2PV	UL3PV	UL4PV
Type	trip	tunnel	tunnel	tunnel	trip	tunnel	tunnel	tunnel
	mass	mass	mass	mass	mass	mass	mass	mass
	ug*	ug	ug	ug	ug	ug	ug	ug
naphthalene	19.5	17.7	25.7	29.3	30.5	37.5	38.6	15.1
2-methyl naphthalene	0.2	0.3	0.4	0.4	0.2	1.7	2.2	2.3
1-methyl naphthalene	0.2	0.3	0.4	0.4	0.2	1.0	1.3	1.3
biphenyl	0.1	0.1	0.1	0.1	0.4	0.4	0.7	0.7
2,6-dimethyl naphthalene	0.3	0.5	0.5	0.4	0.3	0.8	0.9	1.1
acenaphthylene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0
acenaphthene	0.7	0.8	0.7	0.7	0.9	1.3	1.2	1.1
2,3,5-trimethyl naphthalene	1.9	1.9	1.5	1.4	1.4	1.5	1.6	1.6
fluorene	0.6	0.7	0.6	0.5	0.8	0.9	0.8	0.7
1-methyl phenanthrene	0.7	0.3	0.2	0.2	0.2	0.2	0.4	0.2
phenanthrene	3.1	2.0	1.6	1.2	2.3	1.6	2.1	1.8
anthracene	0.6	0.3	0.2	0.2	0.4	0.3	0.4	0.3
fluoranthene	0.2	0.1	0.1	0.0	0.2	0.1	0.1	0.1
pyrene	0.4	0.3	0.1	0.0	0.4	0.2	0.3	0.1

* µg = micrograms per sample

Table 3-10. Blank levels in PUF Samples.

Sample ID:	TR157	UL101	Ul120	UL134	TR1PV	UL2PV	UL3PV	UL4PV
Type:	trip	tunnel	tunnel	tunnel	trip	tunnel	tunnel	tunnel
	mass	mass	mass	mass	mass	mass	mass	mass
	ug*	ug	ug	ug	ug	ug	ug	ug
naphthalene	0.0	0.2	0.2	0.2	0.1	0.1	0.2	0.2
2-methyl naphthalene	0.0	0.3	0.2	0.3	0.1	0.1	0.2	0.2
1-methyl naphthalene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
biphenyl	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
2,6-dimethyl naphthalene	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.2
acenaphthylene	0.0	0.0	0.1	0.1	0.0	0.1	0.2	0.1
acenaphthene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.0
2,3,5-trimethyl naphthalene	0.0	0.1	0.1	0.1	0.0	0.1	0.2	0.1
fluorene	0.0	0.1	0.1	0.0	0.0	0.1	0.1	0.1
1-methyl phenanthrene	0.0	0.2	0.3	0.1	0.0	0.2	0.3	0.1
phenanthrene	0.1	1.0	1.2	0.7	0.1	0.6	1.0	0.4
anthracene	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
fluoranthene	0.0	0.2	0.2	0.1	0.0	0.2	0.5	0.6
pyrene	0.0	0.2	0.2	0.2	0.0	0.2	0.8	1.0

* µg = micrograms per sample

Trip and tunnel blank effects are discussed in the main body of the report. Any sample where the tunnel or trip blank exceeds 20% of the sample values are highlighted in bold.

Calibration standards.

PAH NIST standard reference material 2260 was used for calibration. Deuterated standard were obtained from Cambridge Isotope Laboratories and Accustandards.

Instrument tune

The MS is tuned (calibrated) prior to running a batch of samples.

Multi-point calibration and limit of detection

A 5 point multi-point calibration curve was performed prior to the analysis of each batch of samples. The calibration range was from 25 pg/ul to 1000 pg/ul. R values were .99 or better. The reporting limit was based on the lowest level calibration standard (25 pg/ul) run during the calibration curve.

Reagent Blank

Prior to analysis of a batch of samples a reagent blank is performed to determine PAH background levels in the solvent.

Control

A midpoint calibration standard was run after every 10 samples to determine the instrument drift. If calibration checks differed from the initial calibration by more than 30% the samples were reanalyzed. If the drift exceeded 30% the samples were rerun and analyzed. Sample set run on 6/7/97 exceeded control limit and were reanalyzed. H110X1, H127XL, H145X, H150X, H170 were rerun on 8/28/97 and UL100X, Ul120X, UL134X, and TR157 were reun on 12/22/87.

Sample replicates

For the low volume sampler two diesel exhaust samples were taken for the reformulated and pre-1993 fuel. For the low aromatic fuel one diesel exhaust sample was collected.

For the high volume sampler one diesel exhaust sample per fuel was taken.

Analytical replicates

All samples were analyzed in duplicate except diesel particulate samples H170 and H127 results were based on single analysis.

Instrument Maintenance and Modification summary

Listed in the materials and methods section is the protocol for the analysis of the samples were not run unless the instrument passed tune and was calibrated with a 5 point calibration curve. Columns were clipped when tailing affected calibration or when there was target analytes were not adequately resolved. When tailing did not significantly improve after clipping the column or when the column was to short to adequately separate benz[a]anthracene from chrysene then the column was replaced. Septa and liners and gold seals in the injector were replace routinely during the study.

Summary of Departures

No standardized test method were available for the analysis of diesel samples. Basic test methods were developed by UCD in previous contracts. Protocols are summarized in the materials and methods section and no departures of these protocols were noted. Typically particulate samples are run with a multipoint calibration but since there was only 3 samples a single mid-point calibration standard was run for particulate filter samples H3, H4, H6. Since the multi-point calibration curves are quite stable a mid-point calibration was considered adequate.

Audits and Round Robin

Two laboratories were to conduct PAH analysis. Two determine comparability of the two labs a diesel particulate filter collect by SAPRC during the pre-test was divided in half with one-half sent to UCD for analysis and the other half analyzed by SAPRC. The comparison between the

analysis show good agreement. Results presented in Table 3-11 are in microgram per milligram of diesel particulate matter.

Table 3-11. SAPRC and UCD PAH results of a split diesel particulate filter

PAH	SAPRC (ng/mg)	UCD (ng/mg)
phenanthrene	90	110
anthracene	18	26
Me-phenanthrnes/anthracenes	133	169
fluoranthene	231	262
pyrene	446	556
benz[a]anthracene	97	
chrysene + triphenylene	76	
sum of 228 dalton species*	172	189
benzo[b+j+k] fluoranthene	180	179

* UCD analysis of chrysene, triphenylene, and benz[a]anthracene were not chromatographically resolved and are reported as one number.

UCD and SAPRC interlaboratory comparison High volume sampler. Two laboratories were involved in this study. SAPRC conducted PAH sampling using a high volume sampler consisting of a two filters and PUF sorbant. The sampling was designed to trap PAHs of three rings or more. UCD conducted PAH sampling using both high volume and low volume samplers consisting of two filters, a PUF sorbant and XAD sorbant. UCD was responsible for sampling for volatile PAHs (2-4 ring). The results of the comparison are given in the discussion section in the main body of the report.

3.11 DIOXIN QUALITY ASSURANCE PROCEDURES

Introduction

A screening test for PCDDs and PCDFs was conducted at the MTA facility. PCDD and PCDF analysis was performed by Alta Laboratories. A summary of the QA procedures are given below.

Blanks and Spikes

Laboratory Solvent Blank Prior to analysis of a batch of samples a laboratory solvent blank is performed to determine PCDF and PCDF background levels in the solvent.

Laboratory Method Blanks. Prior to the analysis of a batch of samples a laboratory method blank is analyzed. The method blank is used to determine background levels in the analytical procedure. A suitable matrix is selected for the blank. The blank is then prepped identically to the samples and the blank is analyzed for background contamination. Listed in Table 3-12 is the summary of the matrix used for the method blanks.

Table 3-12. Summary of method blank matrixes for each sample type.

Sample Type	Matrix
Emission	PUF
Tunnel Particulate Matter	Ottawa Sand
Diesel Fuel	Extraction solvent (DCM)
Diesel Oil	Extraction solvent (DCM)

Presented in Table 3-13 are the method blank results. All compound in the method blanks were below the detection with the exception of OCDD. The method and tunnel blanks are discussed in Table IV-7 and are discussed in the body of the report. Concentrations and detection limits are given in picograms per sample.

Table 3-13. Summary of method blank results

Method Blanks

Sample ID:	2950		3160		3214		3257	
Date Analyzed:	10/10/96		12/17/96		12/30/96		1/13/97	
Compound	Conc.	D.L.	Conc.	D.L.	Conc.	D.L.	Conc.	D.L.
2,3,7,8-TCDD	ND	2.2	ND	1.9	ND	2.1	ND	4.5
Total TCDD1	ND	2.2	ND	1.9	ND	3.5	ND	4.5
1,2,3,7,8-PeCDD	ND	2.6	ND	0.68	ND	1.5	ND	5
Total PeCDD	ND	2.6	ND	0.68	ND	1.5	ND	5
1,2,3,4,7,8-HxCDD	ND	2.5	ND	1.1	ND	1.8	ND	5.2
1,2,3,6,7,8-HxCDD	ND	2.2	ND	1	ND	1.8	ND	5
1,2,3,7,8,9-HxCDD	ND	2.4	ND	0.94	ND	1.6	ND	4.7
Total HxCDD	ND	2.5	ND	1.1	ND	1.8	ND	5.2
1,2,3,4,6,7,8-HpCDD	ND	4.9	ND	2.8	ND	1.9	ND	20
Total HpCDD	ND	4.9	ND	2.8	ND	1.9	ND	20
OCDD	10		14		5.7		57	
2,3,7,8-TCDF	ND	4.3	ND	1.5	ND	1.4	ND	6.9
Total TCDF	ND	4.3	ND	1.5	ND	1.4	ND	6.9
1,2,3,7,8-PeCDF	ND	2.9	ND	0.73	ND	1.7	ND	6
2,3,4,7,8-PeCDF	ND	2.9	ND	0.71	ND	1.7	ND	6
Total PeCDF	ND	2.9	ND	0.73	ND	1.7	ND	6
1,2,3,4,7,8-HxCDF	ND	1.2	ND	0.4	ND	0.69	ND	3.2
1,2,3,6,7,8-HxCDF	ND	1	ND	0.35	ND	0.6	ND	2.7
2,3,4,6,7,8-HxCDF	ND	0.86	ND	0.41	ND	0.72	ND	3.2
1,2,3,7,8,9-HxCDF	ND	1	ND	0.47	ND	0.82	ND	3.6
Total HxCDF	ND	1.2	ND	0.47	ND	0.82	ND	3.6
1,2,3,4,6,7,8-HpCDF	ND	3.2	ND	0.87	ND	0.87	ND	4.1
1,2,3,4,7,8,9-HpCDF	ND	4.2	ND	0.67	ND	1.1	ND	5
Total HpCDF	ND	4.2	ND	0.87	ND	1.1	ND	5
OCDF	ND	4.5	ND	2.1	ND	3.2	ND	25

Table 3-13. cont.

Laboratory ID:	3404		3404		3605	
Matrix:	Fuel oil		Carbon		Carbon	
Date Analyzed:	3/5/97		3/5/97		3/5/97	
Compound	Conc (pg/L)	D.L. (pg/L)	Conc (pg/L)	D.L. (pg/L)	Conc. (pg/g)	D.L. (pg/g)
2,3,7,8-TCDD	ND	6.4	ND	2.9	ND	7.9
Total TCDD1	ND	6.4	ND	2.9	ND	27
1,2,3,7,8-PeCDD	ND	3.7	ND	2.6	ND	12
Total PeCDD	ND	3.7	ND	2.6	ND	12
1,2,3,4,7,8-HxCDD	ND	3.7	ND	2.1	ND	21
1,2,3,6,7,8-HxCDD	ND	4.1	ND	2.3	ND	23
1,2,3,7,8,9-HxCDD	ND	3.5	ND	2	ND	21
Total HxCDD	ND	4.1	ND	2.3	ND	23
1,2,3,4,6,7,8-HpCDD	ND	9.4	6.5		ND	26
Total HpCDD	ND	9.4	11		ND	26
OCDD	66		88		150	
2,3,7,8-TCDF	ND	5.1	ND	1.6	ND	9.7
Total TCDF	ND	5.1	ND	1.6	ND	9.7
1,2,3,7,8-PeCDF	ND	6	ND	1.8	ND	15
2,3,4,7,8-PeCDF	ND	5.7	ND	1.7	ND	15
Total PeCDF	ND	6	ND	1.8	ND	15
1,2,3,4,7,8-HxCDF	ND	1.6	ND	2.4	ND	10
1,2,3,6,7,8-HxCDF	ND	1.5	ND	2.2	ND	10
2,3,4,6,7,8-HxCDF	ND	17	17		49	
1,2,3,7,8,9-HxCDF	ND	2	ND	2.6	ND	12
Total HxCDF	ND	17	17		49	
1,2,3,4,6,7,8-HpCDF	ND	2.4	ND	0.95	ND	14
1,2,3,4,7,8,9-HpCDF	ND	3.4	ND	1.3	ND	15
Total HpCDF	ND	3.4	ND	1.3	ND	15
OCDF	ND	6.4	ND	2.9	ND	39

Concentrations and detection limits are given in picograms per liter of sample.

Tunnel Blanks. Two tunnel blanks were collected from the primary dilution tunnel while the CVS fan on the tunnel was turned on and the engine was not running. A tunnel blank was collected prior to diesel exhaust sampling of the reformulated and pre-1993 fuels. Discussion of tunnel blanks is given in IV- 5 of the Results section.

Recovery Spikes. Prior to sampling each sample and tunnel blank is spiked with a mix of isotopically label standards. Recovery of internal standards are considered in perfomance if recoveries are between 60-140%. If recovery of spiked internal standards are low this may indicate some problem in sampling such as breakthrough. Listed in Table IV-12 are the spike recoveries.

Calibration

Certified PCDD and PCDF standards and istopically labeled PCDF and PCDD standards obtained from Cambride Isotope Laboratories were used for calibration and spiking.

To ensure that the GC/HRMS is in control the following procedure is run with each batch of samples.

Initial calibration. Once every six month a 5 point calibration curve is performed to demonstrate linearity and to update the calibration.

Instrument tune. The HRMS is tuned (calibrated) prior to running a batch of samples.

Column performance standard/window define mix. A mix of PCDDs and PCDDs is injected to GC/HRMS to determine if the 2,3,7,8 TCDD peak is adequately resolved (25% valley) from other peaks. The mix also contains the first and last eluting isomer in each MS window to determine that the MS windows are properly set.

Continuing mid-point calibration. A mid-point calibration is performed daily. If the average response factor is within 25% of the initial multipoint average response factor the analysis can begin. If it is outside of the range the problem must be

resolved and the daily calibration must be repeated. If the problem cannot be resolve a new 5 point calibration curve must be conducted.

Method blank. A method blank is run prior to the analysis of a batch of samples.

Laboratory Control Samples. Laboratory control samples like the method blank use a representative matrix similar to the sample analyzed. The matrix is spiked with native PCDDs and PCDFs and the control samples undergo the same analytical procedure as the sample. The relative percent difference between the two control are reported. Listed in Table 3 are the results of the LC samples conducted for these samples.

Control

Presented in Table 3-14 are the laboratory control samples results.

Table 3-14. Summary of Laboratory Control Samples

Laboratory Control Spikes

	10/10/96			12/16/96		
Laboratory ID:	2950			3214		
	LCS1 %R	LCS2 %R	%RLP	LCS1 %R	LCS2 %R	%RLP
2,3,7,8-TCDD	97	95	2.1	90	88	2.2
1,2,3,7,8-PeCDD	100	98	2	98	95	3.1
1,2,3,4,7,8-HxCDD	97	101	4	94	95	1.1
1,2,3,6,7,8-HxCDD	113	106	6.4	97	97	
1,2,3,7,8,9-HxDCC	108	103	4.7	96	97	1
1,2,3,4,6,7,8-HpCDD	98	96	2.1	92	90	2.2
OCDD	102	99	3	94	93	1.1
2,3,7,8-TCDF	93	92	1.1	87	85	2.3
1,2,3,7,8-PeCDF	97	95	2.1	92	91	1.1
2,3,4,7,8-PeCDF	96	95	1	91	87	4.5
1,2,3,4,7,8-HxCDF	96	96	0	99	97	2
1,2,3,6,7,8-HxCDF	108	104	3.8	98	97	1
2,3,4,6,7,8-HxCDF	102	102	0	99	97	2
1,2,3,7,8,9-HxCDF	114	114	0	106	103	2.9
1,2,3,4,6,7,8-HpCDF	99	97	2	91	89	2.2
1,2,3,4,7,8,9-HpCDF	108	110	1.8	95	90	5.4
OCDF	104	101	2.9	92	91	1.1

Table 3-14 cont.

Laboratory Control Spikes

Laboratory ID	12/30/96 3214			1/13/97 3257		
	LCS1 %R	LCS2 %R	RPD% %RLP	LCS1 %R	LCS2 %R	RPD% %RLP
2,3,7,8-TCDD	93	92	1.1	86	89	3.4
1,2,3,7,8-PeCDD	96	95	1	93	89	4.4
1,2,3,4,7,8-HxCDD	92	91	1.1	88	81	8.0
1,2,3,6,7,8-HxCDD	119	109	8.8	93	96	3.2
1,2,3,7,8,9-HxDCC	102	102	0	74	79	6.5
1,2,3,4,6,7,8-HpCDD	97	97	0	95	96	1
OCDD	100	99	0	100	100	0
2,3,7,8-TCDF	90	93	3.3	84	87	3.5
1,2,3,7,8-PeCDF	99	98	1	92	91	1.1
2,3,4,7,8-PeCDF	101	99	2	86	88	2.3
1,2,3,4,7,8-HxCDF	95	99	4.1	91	90	1.1
1,2,3,6,7,8-HxCDF	110	113	2.7	93	94	1.1
2,3,4,6,7,8-HxCDF	106	106	0	69	74	7
1,2,3,7,8,9-HxCDF	110	112	1.8	77	80	3.8
1,2,3,4,6,7,8-HpCDF	101	105	3.9	94	94	0
1,2,3,4,7,8,9-HpCDF	103	109	5.7	90	98	8.5
OCDF	111	118	6.1	111	109	1.8

Table 3-14 cont.

Laboratory Control Spikes

Laboratory ID:	3/5/97 3404			3/4/97 3404		
	LCS1 %R	LCS2 %R	%RLP	LCS1 %R	LCS2 %R	%RLP
2,3,7,8-TCDD	85	88	3.5	86	89	3.4
1,2,3,7,8-PeCDD	100	104	2	94	100	6.2
1,2,3,4,7,8-HxCDD	92	96	4.3	93	95	2.1
1,2,3,6,7,8-HxCDD	93	95	2.1	91	95	4.3
1,2,3,7,8,9-HxDCC	91	93	2.2	89	92	3.3
1,2,3,4,6,7,8-HpCDD	96	99	3.1	93	96	3.2
OCDD	91	95	4.3	91	95	4.3
2,3,7,8-TCDF	89	89	0	89	92	3.3
1,2,3,7,8-PeCDF	95	99	4.1	94	98	4.2
2,3,4,7,8-PeCDF	96	102	6.1	97	100	3
1,2,3,4,7,8-HxCDF	91	93	2.2	90	92	2.2
1,2,3,6,7,8-HxCDF	92	95	3.2	89	93	4.4
2,3,4,6,7,8-HxCDF	88	92	4.4	86	91	5.6
1,2,3,7,8,9-HxCDF	92	95	3.2	90	93	3.3
1,2,3,4,6,7,8-HpCDF	90	93	3.3	88	91	3.4
1,2,3,4,7,8,9-HpCDF	89	92	3.3	88	90	2.2
OCDF	103	108	4.7	108	113	4.5

Table 3-14 cont.

Laboratory Control Spikes

	4/25/97		
Laboratory ID:	3605		
	LCS1 %R	LCS2 %R	RPD% %RPD
2,3,7,8-TCDD	92	98	6.3
1,2,3,7,8-PeCDD	104	110	5.6
1,2,3,4,7,8-HxCDD	90	98	8.5
1,2,3,6,7,8-HxCDD	89	93	4.4
1,2,3,7,8,9-HxDCC	83	93	11
1,2,3,4,6,7,8-HpCDD	96	102	6.1
OCDD	92	98	6.3
2,3,7,8-TCDF	94	99	5.2
1,2,3,7,8-PeCDF	93	100	7.3
2,3,4,7,8-PeCDF	94	99	5.2
1,2,3,4,7,8-HxCDF	96	101	5.1
1,2,3,6,7,8-HxCDF	97	103	6
2,3,4,6,7,8-HxCDF	94	98	4.2
1,2,3,7,8,9-HxCDF	97	105	7.9
1,2,3,4,6,7,8-HpCDF	97	103	6
1,2,3,4,7,8,9-HpCDF	97	104	7
OCDF	102	107	4.8

Replicates

No laboratory replicates were performed however three replicates diesel exhaust samples were collected for the engine using both reformulated and pre-1993 fuel.

Limit of Detection

LODs are based on signal to noise ratio 2.5:1 of the analyte to background noise. LODs are performed on all the analytes for every analysis.

Instrument Maintenance and Modification Summary

No modifications to the methods given in the Chemical Analysis (section C) were made during the study.

Summary of Departure

No departures from methods and protocols listed in the materials and methods section were noted by the Alta Laboratory

3.12 Bioassy Analyses

Introduction

Bioassay analyses were conducted on emission samples from all fuels tested. The bioassay uses bacteria as an indicator organism and detects damage to DNA (genotoxicity) by chemical compounds and complex environmental mixtures. The amount of damage to DNA is reported as the number of mutant organisms, referred to as "revertants".

Blanks

There were a number of blank samples incorporated into the analyses. These were measured to determine any background levels of genotoxic compounds present. The total number of blank samples represented at 1 blank sample for every 3 fuel samples collected and extracted.

Trip blanks – pre-cleaned filters and sorbents that were identical to those used to collect sample were extracted, handled, stored and tested in bioassay exactly as the samples. There were 2 trip blanks extracted.

Field blanks – pre-cleaned filters and sorbents were used to collect blank dilution tunnel samples. Samples were extracted, handled, stored and tested in bioassay exactly as the samples. There were 2 field blanks collected and extracted.

Bioassay method blanks – solvent controls are incorporated into the analyses to determine any background level of genotoxic activity. These are incorporated for each experiment and for every tester organism (TA98 and TA100) tested and for every metabolic enzyme condition tested (with and without S9). A statistical summary of these are provided in the "Controls" section below.

The blanks were handled and tested in an identical procedure as the samples. The trip and tunnel blanks for the particulate matter had activity similar to the negative control values compared to the samples. The trip and field blanks for the vapor-phase samples had little or no activity above that detected in the background samples. Trip and field blank samples for the fractionated PUF samples had measurable levels of activity in certain fractions, due possibly to compounds present in the tunnel, or present in the pre-cleaned C18 or silica SPE columns used.

Calibration

The bioassay is checked for reproducible responsiveness at each analyses by examining a number of factors. The test organisms used are also checked routinely for maintaining specific genes necessary for detecting genotoxic compounds.

Background level of genotoxic activity – is measured with the solvent that is used to dissolve the extract from the filter or sorbent. This is usually dimethyl sulfoxide (DMSO). Each tester strain used has a historical background level of revertants (mutant) organisms.

Level of genotoxic activity with positive controls. – is measured for each tester organism with known genotoxic compounds such as benzo(a)pyrene.

Test of specific genes present in the tester organisms. Known genes called genetic markers are routinely tested with every bioassay. These genes are important for the sensitivity and specificity of the strains.

Compounds or complex mixtures are considered genotoxic if there is a linear dose response curve and if the level of activity is elevated at least 2 times over the background level of genotoxic activity.

Linear dose-response curves were observed for particle and vapor-phase samples. All gene markers for all experiments were normal.

Controls

There are a number of controls used routinely in the bioassay.

Negative control -- or solvent control. As mentioned above, the solvent used to dissolve the genotoxic compounds is tested without additional compounds added to measure the background level of genotoxic activity. Mean (± SD) negative control values for each strain with and without metabolic enzymes added (± S9 added) were:

TA98 (+S9):	16 (± 6), DMSO, n = 10 separate experiments, triplicate plates for each experiment.
TA98 (-S9):	15 (±7), DMSO, n = 9 separate experiments, triplicate plates for each experiment.
TA100 (+S9):	71 (±9), DMSO, n = 7 separate experiments, triplicate plates for each experiment.
TA100 (-S9):	63 (±6), DMSO, n = 8 separate experiments, triplicate plates for each experiment.

Positive control -- or genotoxic compound control. The positive control is routinely tested with each experiment. The positive control is an indicator of the response of the tester strain.

TA98 (+S9):	414 (±41), benzo(a)pyrene, n = 10 separate experiments, triplicate plates for each experiment.
TA98 (-S9):	940 (±43), 2-nitrofluorene, n = 9 separate experiments, triplicate plates for each experiment.
TA100 (+S9):	776 (±99), benzo(a)pyrene, n = 7 separate experiments, triplicate plates for each experiment.
TA100 (-S9):	712 (±13), nitroquinoline-n-oxide, n = 8 separate experiments, triplicate plates for each experiment.

All positive and negative controls were within historical values for this laboratory. The positive controls had standard deviations of 15% or less. The negative controls for TA98 are historically lower than TA100 and were within values normally observed in this laboratory. For example, TA98 (+ S9) had an average background of 16 with SD of 6 (n=10 separate experiments), while TA100 had an average background of 71(+S9) with a standard deviation of 9 for 7 separate experiments. There was one experiment where the background on TA98 was many fold higher than the average. This experiment was repeated and the levels of the background genotoxic activity returned to the average value.

Replicates

Filter and sorbent samples for each fuel were fractionated and each fraction tested in duplicate. All high volume samples represented two consecutive cycles were extracted and tested. Where there is adequate sample for dose-response relationships, at least three doses in duplicate were tested. Positive and negative controls were tested in triplicate for each experiment.

4 Replicate Test Variability

Standard deviations calculated from replicate test data are shown with the emission results data in Chapter 3.0. Table 4-1 shows the pooled estimate of the standard deviations within fuel-type / cycle-type combinations in units of mg/bhp-hr and as a percentage of mean emission rates. The mean rates in this table were obtained by averaging the means of each fuel-type / cycle type combination. The means in this table therefore give equal weight to Cold-Start and Hot-Start emission rates

The table shows that replicate test variability was generally quite low. For species with emission rates above 10 mg/bhp-hr the variabilities range from about 1 to 10%. For the criteria pollutants, the variabilities are slightly larger than the 2% expected based on CFR tolerances, probably indicating small but real variability from run to run. For the remaining species, the run to run variability is about the same or smaller than the variability to be expected from flow rate and analytical precisions, indicating that within the capabilities of the test methods, the runs within a given fuel/cycle type are essentially equivalent.

Table 4-1. Replicate Test Variability

	Mean Rate	Pooled Std. Dev	
Species	mg/bhp-hr	mg/bhp-hr	%
NOx	4692	90	1.9%
THC	490	20	4.0%
CO	2355	111	4.7%
CO2	530567	4828	0.9%
PM	208	11	5.5%
1,3-Butadiene	2.02	0.25	13%
Benzene	6.69	0.72	11%
Toluene	2.08	0.32	15%
Ethylbenzene	0.92	0.53	58%
o-xylene	0.78	0.14	18%
m&p-xylene	1.76	0.39	22%
Styrene	1.45	0.56	39%
Naphthalene	1.48	0.34	23%
Nitrate	0.21	0.05	22%
Sulfate	0.70	0.39	55%
Ammonium	0.44	0.11	25%
Organic Carbon	62.10	6.68	11%
Elemental Carbon	117.69	10.78	9%
Mg	0.07	0.04	55%
Si	0.64	0.10	16%
P	0.08	0.02	29%

S	0.89	0.12	14%
Cl	0.03	0.02	46%
Ca	0.07	0.03	52%
Fe	0.27	0.16	59%
Cu	0.01	0.01	111%
Zn	0.16	0.05	29%
formaldehyde	58.72	3.11	5%
acetaldehyde	19.17	0.97	5%
acrolein	3.43	1.10	32%
acetone	6.43	0.76	12%
propionaldehyde	4.04	0.48	12%
crotonaldehyde	1.71	0.38	22%
methacrolein	0.09	0.27	-
MEK	0.00	0.00	-
butyraldehyde	4.08	1.32	32%
benzaldehyde	1.74	0.83	48%
valeraldehyde	0.82	0.18	23%
tolualdehyde	3.38	0.99	29%
hexaldehyde	0.47	0.14	30%

5 Adequacy of Data for Intended Purpose

All data capture criteria were met. External audits for criteria gases found one problem, but the cause of the problem was identified, corrective actions were taken, and corrected data met audit tolerances. External audits for flow rates were satisfied. Accuracies and precisions met goals. Within fuel/cycle type, variability was low. Computerized data calculations were checked and agreed with results using manual calculations. Raw data to support the results of the study are archived.

No problems have been identified that would affect the adequacy of the data for its intended purpose.

6 References

ARB, 1996. Audit report memo by Kamal W. Abdul-Karim dated 5/22/96, with audit test results. Air Resources Board, El Monte, CA.